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The Fibers' Christmas Eve

'Twas the night before Christmas, and all through the house
Not a creature was stirring, not even a mouse.
The stockings were hung by the chimney with care
In hopes that new nylons would give far more wear.
The fibers all snuggled asleep in their beds,
While visions of "wash and wear" danced in their heads.
And Ma's cotton nightie and Dad's new silk tie
Were dreaming of finishes, stitching, and dye.
The resins were planning a crease-holding spree
And fireproof draperies were hung by the tree.
When all of a sudden there came such a clatter
That all of the fibers cried "Oh—what's the matter?"
'Twas only Saint Nicholas, out on the roof
With gifts for the little ones, warp and the woof!
For rayon, a new dye for both skin and core,
For cotton, old Santa had presents galore!
Ramie, and cashmere, and wool and the others
Shared in the presents with new manmade brothers.
The Santa?—you've guessed him—he's fiber research—
The "ivory tower" is his lofty perch.
Without him the world couldn't say with such cheer
Merry Christmas to all—and a Happy New Year!

CANDY FRENKING

TEXTILE RESEARCH JOURNAL

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Application of Statistical Theory of Elastomers to Supercontracted Keratin Fibers

A. R. Haly and M. Feughelman

Physics and Engineering Unit, Wool Textile Research Laboratories, Commonwealth Scientific and Industrial Research Organization, The Hermitage, Ryde, N.S.W., Australia

Abstract

Supercontraction in lithium bromide solutions of wool, human hair, and kid mohair takes place in two distinct stages. Evidence is presented which suggests that the polypeptide chains in these fibers, after supercontraction in lithium bromide solution, reach a condition both at the end of the first contraction stage and at the end of the second stage when the chain segments between positions of cross-linking approximate a random configuration.

The mean number of amino acid residues in the chains between positions of cross-linking was calculated from degree of contraction data, assuming that the chains were randomly kinked. In addition, the number was calculated from stress–strain data, using a formula which has been derived for rubber. The values obtained in these two ways were in satisfactory agreement.

The nature and distribution of cross-linkages are briefly considered, and it is pointed out that the results are consistent with cystine analyses of the fibers.

Introduction

Elöd and Zahn [6] reported that some keratin fibers, under conditions in which supercontraction takes place, behave as rubber-elastic systems, and that the driving force which causes the fibers to contract results mainly from entropy effects. They remarked that final clarification of the causes of supercontraction and set would be synonymous with a knowledge of the magnitude of the individual chains of high molecular weight, the nature and location of the functional groups and branches, their reactivity and mutual attraction or repulsion, and a number of other factors.

Following a study of the supercontraction of keratin fibers in lithium bromide solutions and of some mechanical properties of supercontracted fibers, we are in substantial agreement with these authors.

The purpose of this paper is to outline the results obtained and to indicate how data about supercontracted protein fibers may help to elucidate their molecular structure.

Materials and Methods

Measurements of rate of contraction and equilibrium contraction were done with the aid of a microscope equipped with a stage heater. The full

length of fiber snippets was measured, the initial length of the snippets varying between 0.5 and 2.0 mm. Three concentrations of LiBr were used: 6.3 *M*, 8.3 *M* and 10.4 *M*.

For mechanical tests, fibers were contracted at approximately 100° C. in 8.3 *M* LiBr for a time sufficient to cause maximum reduction in length. Unnecessary heating under these conditions was avoided, since prolonged treatment causes serious fiber degeneration. After contraction a fiber was mounted in an extensometer and immediately re-immersed in the LiBr solution. Enough time was allowed for equilibrium between fiber and solution to be re-established before mechanical tests began.

The fibers used were Corriedale wool, human hair, and kid mohair. Samples of the two latter types were kindly supplied by Dr. Menkart of the Textile Research Institute, Princeton. All fibers were selected to be medulla-free.

Results

Rates of Supercontraction and Equilibrium Contractions

Curves relating time of heating in LiBr solutions at 89 ± 1° C. and extent of supercontraction were obtained for the three types of fibers. All showed a two-stage contraction (Figure 1), the first stage commencing just before the fiber was completely penetrated by the reagents. After an intermediate period of little or no contraction, a second period of contraction ensued, during which a considerable reduction in length took place. At 100° C. the intermediate stage was more difficult to detect, but it was apparent under some circumstances.

The evidence obtained to date suggests that, with identical keratin material, there is little difference between the degrees of contraction at the intermediate stage whether the reaction takes place at 89° C. or 100° C., in any of the three concentrations of LiBr. The final contraction obtained at 89° C. was less than that at 100° C., but at approximately 110° C. the contraction was no greater than at 100° C. Final contraction at 100° C. was the same in each of the three solutions.

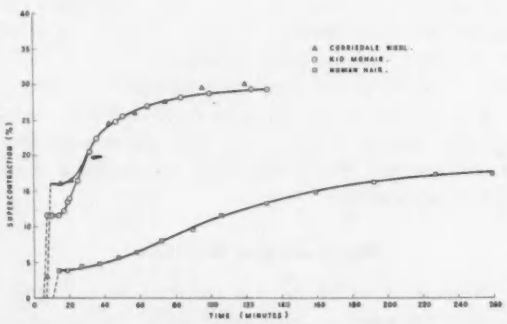

Fig. 1. Supercontraction–time curves for various keratin fibers in 8.3 *M* LiBr at 89° C.

To investigate these points it was necessary to use adjacent snippets from the same fibers. The degree of contraction at the intermediate stage and at equilibrium, as well as varying with fiber type, may vary from fiber to fiber within the same type. Intra-fiber variation was also found. Fiber-to-fiber variation was greatest for intermediate stage contraction in kid mohair. For instance, one kid mohair fiber yielded a value of 11.6 ± 0.5% supercontraction at this stage, while another fiber from the same sample yielded a value of 18.7 ± 0.5%. Figures of comparable accuracy for intermediate stage contraction were not obtained for wool because the snippets coil during contraction, and measurements must therefore be made on photographs. It was not always possible to take these photographs at the most suitable times. It was apparent, however, that the value was about 15%.

Equilibrium contraction of wool at 100° C. determined from six experiments was 41%; the individual values ranged from 39.5 to 41.5%. These figures are the means of measurements made around both the outside and the inside of the curved snippets.

Degree of contraction data are collected in Table I.

If a fiber was removed from the solution before or during the intermediate stage its length was fully restored by washing in water. If, however, it was removed and washed subsequent to this stage its length was at best only partially restored. In the latter part of a contraction experiment, washing a fiber results in further contraction.

Rubber-Elasticity of Supercontracted Fibers

As was mentioned above, Elöd and Zahn [6] found that, under certain conditions, keratin fibers exhibited rubber-like elasticity. For the purposes of the present work this result was checked in the following way: a fully supercontracted fiber mounted in an extensometer and immersed in the supercontracting solution was maintained at a fixed strain.

Stress was then measured at a series of temperature values between 30° and 50° C. Experiments were done using both wool and human hair; as Figure 2 shows, in both cases the stress increased to a good approximation linearly with increase of absolute temperature. Furthermore the straight line extrapolated to zero stress at zero on the absolute temperature scale. This is a characteristic property of a pure elastomeric system.

Modulus of Elasticity of Supercontracted Fibers

Equilibrium stresses at various strains in supercontracted fibers immersed in LiBr solution were determined for both human hair and Corriedale wool. Moduli of elasticity may be calculated using the formula given by Treloar [14], $f = G(\alpha - 1/\alpha^2)$, where G = elastic modulus, $\alpha = 1 +$ strain, and f = force per unit area exerted on the fiber, the area taken being that at zero strain. Here the area used was obtained from diameter measurements made after the fiber was washed in water while it was still immersed. The reason for this will be indicated in the next section.

In Figure 3, f is plotted against $(\alpha - 1/\alpha^2)$. It will be seen that G was found to increase as the strain increased, and that the slope of the curve for human hair was everywhere greater than that for wool.

Discussion

A basic postulate on which this discussion rests is that the macroscopic phenomenon of supercontraction results from a reduction in effective length of the polypeptide chains in keratin, due to their taking up a more probable, shorter configuration after the rupture of constraining bonds by the LiBr.

It is possible that the portions of the chains between positions of cross-linking become randomly kinked, both at the intermediate contraction stage and at final equilibrium. Under these circumstances we would have to assume that some of the linkages which restrict contraction to the intermediate stage value are unstable to the treatment. When these links are destroyed a longer chain is permitted to

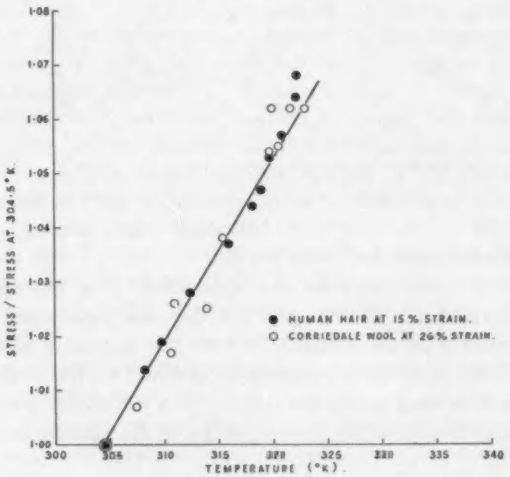

Fig. 2. Effect of temperature on stress in supercontracted fibers; the straight line is drawn through one experimental point, and has a slope such that it would pass through the point indicating zero stress at zero on the absolute temperature scale.

TABLE I. A Comparison Between Cystine Content, Degree of Contraction, and the Calculated Number of Free Links Between Positions of Cross-Linking for Various Fibers

Fiber	Degree of contraction		Value of n 1.67Å*	Value of n 1.5Å*	Value of n Mechanical test	Cystine content (by weight)
Human hair	Intermediate	3.5– 5%†	10	13	—	
	Maximum	21–23%‡	16	20	18	17.0%
Wool	Intermediate	~15%	14	17	—	
Corriedale	Maximum	41%	28	34	25	9.6%
Kid mohair	Intermediate	11.6–20%†	12–15	15–19	—	
	Maximum	40–44%§	29	36	—	9.6%

* The projected axial residual length used a basis for the calculation.
† The error in measurement did not exceed 0.5%.
‡ The mean of twelve measurements was 21.7%.
§ The mean of eleven measurements was 42.2%.

become randomly kinked; i.e., there is further contraction.

There is some evidence that these events take place. It has been shown that supercontracted fibers, saturated with the supercontracting medium, exhibit rubber-elasticity. This implies that the stress in a stretched fiber results entirely or almost entirely from entropy effects. Such a fiber, released from external constraints, should contract until entropy reaches a maximum; i.e., until the chains become randomly kinked. Chain entanglements or cohesive forces within the fiber may prevent this configuration being achieved. In this case, however, it would be expected that an increase in temperature would tend to overcome these restraints and allow a greater degree of contraction. It is therefore significant that the degree of contraction at the intermediate stage was unaffected by an increase of temperature above 89° C. and that the final degree of contraction was unaffected by an increase from 100° to about 110° C., in both cases indicating that a randomly-kinked state had been attained.

We may consider the application of a formula derived by Eyring [7] for the root-mean-square value r of the distance between the ends of a randomly kinked molecular chain in which all the bonds and valence angles are equal. To a sufficiently good approximation for present purposes the formula is

$$r^2 = nl^2 \frac{1 + \cos\theta}{1 - \cos\theta} \qquad (1)$$

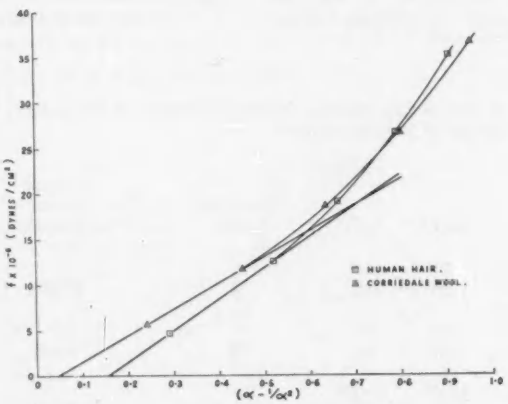

Fig. 3. Graph showing the relationship between f and $(\alpha - 1/\alpha^2)$ for supercontracted fibers. The straight lines join the first two experimental points in each case. $\alpha = 1$ + strain.

where n = number of links in the chain, l = length of a link, and θ = the semi-angle of the cone swept out by rotation of the links in the chain.

In applying this formula to supercontracted keratin fibers, it will be assumed (see Corey and Pauling [4]) that there is no rotation about the bond between the HN–CO groups in the polypeptide chain, and therefore that the length of a link in the chain is a residue length. Further, it will be assumed that the fundamental dimensions and valence angles of the polypeptide chains are the same in both crystalline and amorphous regions of the fiber.

The residue length l will be taken as 3.67Å (Astbury [2]) and θ as 70° [4].

We now require a value for r^2. Extended keratin fibers show an X-ray diffraction spot corresponding to a repeat distance of about 3.33Å [2], and this value will be taken as the projected length of a residue in the axial direction when the chains are extended as far as possible without valence angle change. It has been reported [9, 15] that keratin fibers can be extended 100% from their natural length without breaking peptide linkages. Thus the average projected residue length, on this basis, when a fiber is in its natural state will be 1.67Å.

Again, X-ray evidence for unstretched keratin fibers (α-keratin) indicates an axial repeat of 1.5Å, which has been interpreted as the projected residue length in the axial direction. Either of these figures of 1.67Å or 1.5Å used in conjunction with the degree of supercontraction enable us to calculate a value of r.

If the projected residue length in the supercontracted state is x, then

$$r^2 = n^2x^2 \qquad (2)$$

Equations 1 and 2 then lead to

$$n = \frac{l^2}{x^2}\left(\frac{1 + \cos\theta}{1 - \cos\theta}\right) \qquad (3)$$

The case of human hair will be considered first because Dusenbury and Jeffries [5] believe that this fiber has only one type of cortical cell, whereas it is known that both wool and kid mohair [8] have two types of cortical cells. Since the maximum contraction obtained with hair was 22%, the projected residue length in the supercontracted state will be 0.78 times the value in the natural state. This leads to a value of $n = 16$ or 20, depending on whether 1.67Å or 1.5Å is taken as the projected residue length for the uncontracted fiber. At the

intermediate stage the degree of contraction of human hair was about 4.3%. This corresponds to a value of $n = 10$ or 13.

This analysis, then, indicates that there are cross-linkages stable to heating at 100° C. in 6.3 *M*, 8.3 *M*, or 10.4 *M* LiBr solution about every twenty residues along the polypeptide chains in human hair. In addition, about half way between these there may be cross-linkages which are unstable to the treatment, and which are broken, permitting the onset of the second stage of contraction. In considering the nature of these linkages, it is to be noted that Elöd and Zahn [6] obtained over 40% contraction by wool in phenol at 100° C. without loss of cystine. Since the maximum contraction of wool in this work was about 41%, it is improbable that the unstable linkages, whether or not they are cross-linkages, involve cystine. It should be mentioned that the activation energy for the second stage of contraction, calculated from rates of contraction at 89° C. and 100° C., was found to be about 30 kcal. per mole for both kid mohair and human hair. This value was independent of the concentration of the lithium bromide solution. It is nearly the same as that found by Ripa and Speakman [11] for long-term creep in wool, and by Rigby [10] for long-term stress-relaxation.

For Corriedale wool an intermediate contraction stage was shown to exist at about 15% contraction; the maximum contraction was 41%. The corresponding values of n are 14 or 17 and 28 or 34. For one kid mohair fiber the intermediate stage occurred at approximately 11.6% contraction, and the maximum contraction was again 41%. This leads to the corresponding values of n of 12 or 15 and 28 or 34. It must be emphasized that because Corriedale wool and kid mohair have two corticular segments these values of n are averages over the two segments.

Effect of Cystine Content

Because a place must be found for cystine in the structure, and because destruction of cystine allows increased contraction, or the same degree of contraction at a lower temperature [6], it seems reasonable to postulate that cystine cross-links are involved in the stable "vulcanization" sites. If now we take the mean of the two values of n (Table I) for hair at maximum contraction, and assume that there is one cystine cross-link at each vulcanization site, we conclude that there is one cystine residue in a total of 19 residues (53 in 1000). For wool the corresponding value is 1 cystine in a total of 32 residues (31 in 1000). The cystine content of Corriedale wool [13] and kid mohair [12] is about 9.6%, and of human hair [12] about 17% by weight. Thus only $\frac{1}{3}$ to $\frac{1}{4}$ of the total cystine in both wool and hair has been accounted for. There is an implication here which can be shown directly as follows:

$$\frac{\text{Total wool cystine}}{\text{Total hair cystine}} = \frac{9.6}{17} \sim \frac{31}{53}$$

That is, even though only a fraction of total cystine has been accounted for on the assumptions so far employed, the ratio of total wool cystine to total hair cystine is the same as the calculated ratio. It is possible that there are two or more cystine links close together at each vulcanization site. Again, Carter et al. [3] have shown that wool cystine occurs in two main fractions of different reactivity, a fraction (A + B) comprising two similar subfractions A and B, and a fraction (C + D) comprising the similar subfractions C and D. The quantity of fraction (A + B) is the same as the quantity of (C + D). It may be that only one of the two main fractions is concerned in cross-linking of polypeptide chains.

This concept and the idea that there may be more than one cystine cross-link at each vulcanization site are not mutually exclusive. Either or both could be consistent with the result (Alexander and Hudson [1]) that destruction of cystine in wool by peracetic acid, followed by treatment in boiling water, causes *no* supercontraction until approximately 50% of the cystine has been oxidized.

It should also be noted that, in the previous discussion, we have assumed that the line joining the vulcanization points at the ends of a random chain is in the direction of the fiber axis. This means that the measurement r is assumed to be in the direction of the fiber axis. Some randomization of the direction of r is to be expected. Perfect randomization would decrease the average axial component of r to a theoretical value of 0.5 r. This would hardly be expected, but the effect of some lack of axial orientation of r would be to reduce the calculated value of n, i.e., to increase the calculated cystine content. Part of the discrepancy between the cystine content estimated above and the value obtained by chemical analysis may be explained in this way.

Stress as a Function of Molecular-Chain Length

There is available another means of arriving at a value of n. Formulae have been derived connecting the modulus of elasticity of a rubber with its chain molecular weight. A formula which has been shown to be a reasonable approximation [14] is

$$G = g\rho RT\left(\frac{1}{M_c} - \frac{1}{M}\right)$$

where g = a constant which has been found to have a value of about 2.5 for highly cross-linked rubber, ρ = density of fiber (the value used will be 1.27, the density of water-saturated wool, since G was calculated using the diameter of the water-saturated fibers), R = the gas constant per mole, T = the absolute temperature, M_c = the formula weight of the chain between vulcanization sites, and M = the true molecular weight. We shall assume that $M \gg M_c$, i.e., $\frac{1}{M}$ is negligible compared with $\frac{1}{M_c}$, so that

$$G = \frac{g\rho RT}{M_c}$$

It seems clear that the appropriate value of G to use here is that at low strain. This is because rubbers deviate more and more from theoretical behavior as the strain increases and because complications due to the presence of LiBr in the fiber are probably least at low strains. In view of the fact that heating keratin fibers in LiBr causes their progressive degeneration, it is better to obtain G from the early slope of the $f\,v\,(\alpha - 1/\alpha^2)$ plot rather than from any particular corresponding values of these quantities. The slopes of the straight lines joining the first two experimental points (Figure 3) yielded $M_c = 1970$ for human hair and $M_c = 2800$ for Corriedale wool. The average residue weight for keratin is about 111, so that $n = 18$ for human hair and 25 for wool.

Since the value of g is uncertain, the mechanical properties of the fibers are affected by the supercontracting treatment, and G was found to increase with increasing strain, this method of obtaining n is unlikely to be accurate. Under the circumstances, the results are in satisfactory agreement with those obtained from degree of contraction data.

Table I presents a comparison for human hair, kid mohair, and Corriedale wool of the relation between cystine content, percentage supercontraction, and the corresponding values of the number of the links between cross-links.

While it is recognized that these types of analysis present many difficulties, particularly in the case of keratin fibers, it is believed that the results are sufficiently encouraging to allow optimism about the future of the methods. Greater precision may be achieved using collagen, silk, regenerated protein fibers, and other materials of more homogeneous composition than keratin fibers.

Literature Cited

1. Alexander, P. and Hudson, R. F., *Wool: Its Chemistry and Physics*, Chapman and Hall Ltd., London, p. 82 (1954).
2. Astbury, W. T., *Proc. Roy. Soc.* **B141**, 1 (1953).
3. Carter, E. G. H., Middlebrook, W. R., and Phillips, H., *J. Soc. Dyers Colourists* **62**, 203 (1946).
4. Corey, R. B. and Pauling, L., *Proc. Roy. Soc.* **B141**, 10 (1953).
5. Dusenbury, J. H. and Jeffries, E. B., *J. Soc. Cosmetic Chemists* **6**, 356 (1935).
6. Elöd, E. and Zahn, H., *Melliand Textilber.* **30**, 17 (1949).
7. Eyring, H., *Phys. Rev.* **39**, 746 (1932).
8. Fraser, R. D. B. and Macrae, T. P., TEXTILE RESEARCH JOURNAL **26**, 618 (1956).
9. Meredith, R., *The Mechanical Properties of Textile Fibres*, North Holland Publishing Company, Amsterdam, pp. 162, 174 (1956).
10. Rigby, B. J., *Australian J. Physics* **8**, 176 (1955).
11. Ripa, O. and Speakman, J. B., TEXTILE RESEARCH JOURNAL **21**, 215 (1951).
12. Simmonds, D. H. (private communication).
13. Simmonds, D. H., *Australian J. Biol. Sci.* **8**, 537 (1955).
14. Treloar, L. R. G., *The Physics of Rubber Elasticity*, Oxford University Press (1949).
15. Woods, H. J., *Physics of Fibres*, The Institute of Physics, London, p. 65 (1955).

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Sources of Errors in the Measurement of Yarn Tensile Forces With a Combination of Mechanical and Electronic Components

Lars Waesterberg

Swedish Institute for Textile Research, Gothenburg, Sweden

Introduction

The measurement of yarn tensile forces is a very common problem in the investigation and control of different yarn processes. The tensile forces introduced in the yarn during a process can be considered as the sum of the effects of many sinusoidal force components of different frequencies. In order to record all of the force conponents correctly, outstanding frequency response characteristics would be required on the part of the measuring device. The various devices commonly used in yarn force measurement differ widely in this respect. A purely mechanical device can hardly be made to give good frequency response characteristics, whereas a purely electronic device might be made to do so. Existing equipment makes use of a combination of mechanical and electric components. The necessary mechanical component is represented by a member suspended by the spring of a force-measuring transducer. The yarn force is generally transmitted to this member by forming a suitable loop on the yarn (Figure 1). The electronic component usually consists of an oscillator, an amplifier, and an indicating or recording device (cathode ray oscillograph + camera). However, a penrecorder is very often used, thus providing another mechanical component formed by the galvanometer loop and the pen. With this combination, the overall frequency response characteristics may be limited either by the inertia of the transducer spring system or by the recording system.

A second important requirement which must be put on the measuring device is that the dynamic conditions on the yarn should not be changed because of the presence of the measuring device; this factor has often been overlooked. In most devices pulleys are considered as suitable means of forming the necessary yarn loop. However, it will be shown here that pulleys can change the dynamic conditions on the yarn appreciably and thus cause various types of errors during such measurements.

Free Vibrations in a System of a Stationary Yarn and a Pulley

Theory

A simple vibration system consists in general of a body that is constantly acted upon by a restoring force acting toward an equilibrium position.

Such a system is represented in Figure 2 by a ball with the mass m suspended from a spring. The force F necessary to accelerate the mass is, according to Newton's law:

$$F = m\ddot{x} \tag{1}$$

where x is the deflection from the equilibrium position.[1]

This force must be in equilibrium with the spring force, which may be written

$$F = kx \tag{2}$$

where k is known as the spring constant. Thus we get from Equations 1 and 2

$$m\ddot{x} + kx = 0 \tag{3}$$

which is the differential equation of motion for the described system when free undamped vibrations occur.

In all practical applications a vibration of this type should be counteracted by damping forces, which cause the amplitudes of the body to decline more and more. Damping may be caused by internal friction in the spring or by friction between the body and air particles, liquids, or solids. The damping force is in most cases proportional to the velocity $\dot{x}\left(=\frac{dx}{dt}\right)$ of the vibration, so if the damp-

[1] $\ddot{x}$ is the second derivative of x; $\ddot{x} = \frac{d^2x}{dt^2}$.

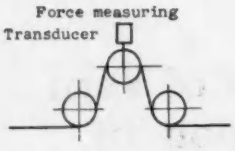

Fig. 1. A three-pulley system for yarn force measurement.

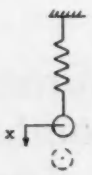

Fig. 2. Vibrating system with one mass and one spring.

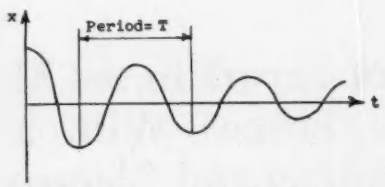

Fig. 3. Graphical representation of a free damped vibration.

Fig. 4. Vibrating system with one mass between two springs.

ing constant is r, the equation of motion is written

$$m\ddot{x} + r\dot{x} + kx = 0 \tag{4}$$

The solution of this equation represents a sinusoidal motion (if damping is not too heavy), with a frequency characteristic for a given system, i.e., the resonant or natural frequency. Such a free damped vibration is represented in Figure 3.

The cyclic frequency is here defined as the number of vibrations per second (ν), where

$$\nu = \frac{1}{T} \tag{5}$$

when ν is the frequency and T is the period. The angular frequency (ω) of a sinusoidal motion, which is expressed in radians/sec., is then given by

$$\nu = \frac{1}{2\pi} \cdot \omega \tag{6}$$

The simple system of Figure 2 can be enlarged to the system in Figure 4, where the body slides on a plane. With the spring constant k for each of the springs, the equation of motion can be written

$$m\ddot{x} + r\dot{x} + 2kx = 0 \tag{7}$$

i.e., the changes in the spring forces are additive.

A similar system is represented by a yarn stretched over a pulley (Figure 5). The two parts of yarn with the length l act as springs with the spring constant k. The friction forces between the yarn and the pulley give a certain degree of coupling. If the pulley is rotated slightly from its equilibrium position without slippage between the yarn and pulley and then suddenly released, a free damped vibration of the type shown in Figure 3 will result.

Using the symbols mass of pulley = m, radius = R, angular deflection = θ, and mass moment of inertia = J, the vibration is represented by the equation of motion as given below:

$$J\ddot{\theta} + r\dot{\theta} + 2k\,R^2\theta = 0 \tag{8}$$

With $J = \frac{1}{2}\,mR^2$ it takes the form

$$\tfrac{1}{2}\,mR^2\ddot{\theta} + r\dot{\theta} + 2kR^2\theta = 0 \tag{9}$$

The solution of this can be found in any of a number of well-known books on mechanical vibrations or differential equations.

The general solution of (9) is

$$\theta = A\,e^{\lambda_1 t} + B\,e^{\lambda_2 t} \tag{10}$$

If the damping is small, this represents a free damped vibration, given by

$$\theta = \theta_0 e^{-at} \cos\,(\omega_d t - \psi) \tag{11}$$

where the resonant frequency = ω_d

$$\omega_d{}^2 = \omega_0{}^2 - a^2 \tag{12}$$

Here

$$\omega_0{}^2 = \frac{4k}{m} \tag{13}$$

where ω_0 is the resonant frequency of the undamped system. The damping factor a is obtained from

$$a = \frac{r}{mR^2} \tag{14}$$

Usually the damping in a system is indicated with

$$\delta = \frac{2a}{\omega_0} \tag{15}$$

The amplitude decreases in accordance with

$$\theta_{0t} = \theta_0\,e^{-at} \tag{16}$$

where θ_0 is the amplitude at time $t = 0$.

Different lengths of the yarn parts (Figure 6) will give different spring constants of the two parts; thus the equation of motion takes the form

$$J\ddot{\theta} + r\dot{\theta} + R^2\theta\,(k_1 + k_2) = 0 \tag{17}$$

Fig. 5. System of a yarn and a pulley.

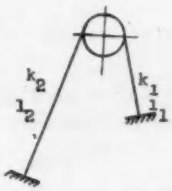

Fig. 6. Yarn and pulley system with different lengths of the yarn parts.

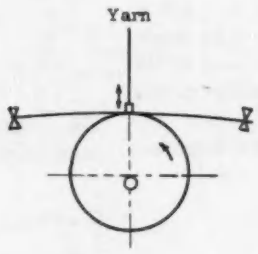

Fig. 7. Mechanical vibrator.

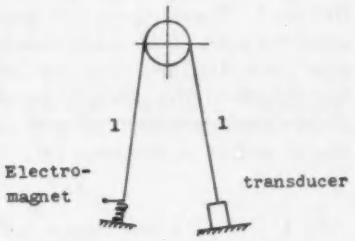

Fig. 8. Determination of the resonant frequency in a yarn and pulley system.

Without damping, the natural frequency will be

$$\omega_0^2 = \frac{2\,(k_1 + k_2)}{m} \tag{18}$$

Experimental

During the experiments to verify the theoretical formulas mentioned above and during the measurements of yarn tensions in several yarn winding processes, the following measuring equipment was used: transducers (resistive and inductive), a bridge and amplifier, and recording galvanometers. Other apparatus included pulleys, a mechanical vibrator, and an electromagnet with armature.

The principle of a resistive transducer is so widely known that it need not be mentioned here. Here the Statham strain gauge, model G1, was used. In the inductive transducer (the linear, variable, differential transformer), the induced voltage depends on the position of a steel core in the center hole of a cylindrical transformer with two secondary coils symmetrically arranged on both sides of a primary coil. This device has been described in textile literature by Barach [1]. The signals from the devices were amplified and sent to a recording galvanometer. Three galvanometers were used—two pen recorders (Brush and Kelvin Hughes) with a frequency response of about 50 and 60 vib./sec. respectively and one jet-recorder (Elema[2]) of about 500 vib./sec.

The pulleys were made of light metal with a press-fitted steel spindle, running in two ball bearings, or, in some cases, jewel bearings.

[2] Made in Sweden.

The following pulleys were used in this work:

Pulley	Radius	Weight
A	6 mm.	1.68 g.
B	6 mm.	1.81 g.
C	10 mm.	4.65 g.

The mechanical vibrator was used to force longitudinal vibrations in a system of yarn and pulleys. The yarn was fastened to a flat spring, which was pressed against an eccentric disc (Figure 7), driven by an electric motor with variable speed. This provided a sinusoidal motion in the yarn with a constant maximum amplitude of 0.5 mm. up to at least 100 vib./sec.

Free vibrations in systems of yarn and pulleys were introduced by fastening one yarn end to the armature of an electromagnet, thus giving it a very rapid elongation of about 2 mm. when the current was switched on to the magnet.

The yarn used during the experiments was viscose rayon 120/30 den.

To determine the resonant frequency in a system of a yarn and a pulley, one yarn end was fastened to the armature of the electromagnet and the other end to a transducer spring (Figure 8). The yarn could be given different pretensions. The resonant frequency was calculated from the recorded sinusoidal force curves.

The pulleys *A* and *C* were used. The spring constant of the yarn was calculated from

$$k = \frac{E \cdot y}{l} \tag{19}$$

where E = Youngs modulus, y = yarn area, and l = yarn length. The following physical constants[3]

[3] p = pond, the force due to the acceleration of gravity acting on 1g.

were used: $E = 12 \times 10^7$ p/cm². and $y = 8.9 \times 10^{-5}$ cm.² The damping was determined by measuring the ratio of one amplitude to the next in the yarn force diagram. However, the damping was very slight in this system, so the resonant frequency could be calculated with a good approximation according to Equation 13.

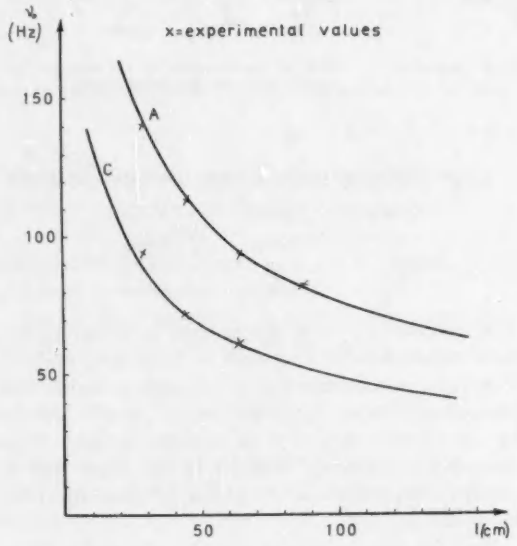

Fig. 9. ν_0 versus l curves for systems of yarn and pulleys A and C. (Hz = 1 vib./sec.)

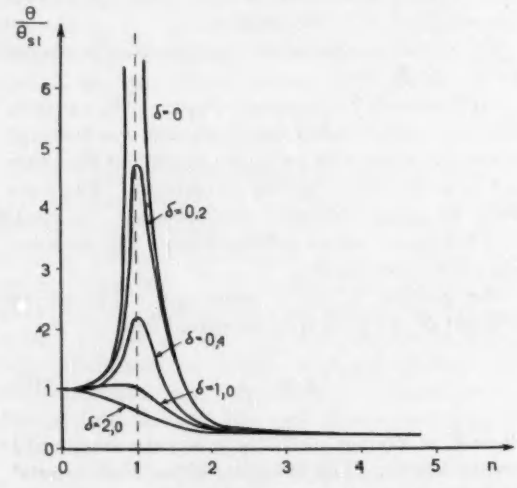

Fig. 10. Ratio of amplitude magnification to frequency with different degrees of damping.

For a certain pulley (constant m) we find

$$\nu_0 = \frac{1}{2\pi} \cdot \omega_0 = \text{constant} \cdot \sqrt{k} = \frac{\text{constant}}{\sqrt{l}} \quad (20)$$

The constant was then calculated from a diagram value of the resonant frequency.

	Pulley A	Pulley C
Value of constant	766	483

Figure 9 shows the theoretical ν_0 versus l curves based on the values of the constant as well as some experimental values of ν_0.

The following conclusions can be drawn from Equations 12, 18, and 20:

1. the resonant frequency decreases with longer yarn parts
2. the resonant frequency decreases with a heavier pulley
3. the resonant frequency decreases with greater damping in the system.
4. with constant total yarn length, the resonant frequency is at minimum when the yarn parts have equal length.

Forced Vibrations in a System of a Yarn and a Guide Pulley

General

Forced vibrations were induced in a yarn system with the mechanical vibrator. One yarn end was fastened to the vibrator spring and the other end to a transducer (Figure 11). With a constant maximum amplitude $= \pm x_{st}$ of the vibrator spring, the equation of motion can be written

$$J\ddot{\theta} + r\dot{\theta} + kR[R\theta + (R\theta - x)] = 0 \quad (21)$$

$$J\ddot{\theta} + r\dot{\theta} + 2kR^2\theta = kRx \quad (22)$$

If the vibrator spring motion is sinusoidal, Equation 22 can be transformed into

$$J\ddot{\theta} + r\dot{\theta} + 2kR^2\theta = kR\,x_{st} \cos \omega t \quad (23)$$

The general solution of this is

$$\theta = \theta_0 e^{-at} \cos(\omega_d t - \psi) + \frac{kRx_{st} \cos(\omega t - \varphi)}{\sqrt{r^2\omega^2 + (J\omega^2 - kR^2)^2}} \quad (24)$$

The first term represents the damped free vibration as given in Equation 11. This term has an influence only at the beginning of the forced vibration, which in the stable form is represented only by the second term.

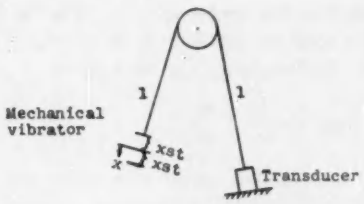

Fig. 11. Forced vibrations are induced in a yarn and pulley system with a mechanical vibrator.

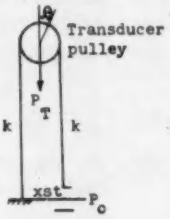

Fig. 12. Reactions in a transducer pulley due to yarn and pulley vibration.

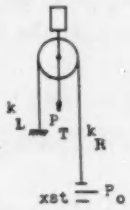

Fig. 13. Reactions in a transducer pulley with different lengths of the yarn parts.

Fig. 14. Vibrating coupled system with two masses and three springs.

φ is the phase angle between the steady sinusoidal motions of the vibrator and the pulley.

Amplitude Magnification

A static displacement x_{st} of the vibrator spring corresponds to a rotatory motion θ_{st} of the pulley. When the pulley (and yarn) is forced into sinusoidal vibrations, the amplitudes θ can be magnified. Maximum magnification θ_0 occurs when the vibrator frequency (ω) equals the resonant frequency of the yarn and pulley system (ω_0), i.e., $n = 1$, where $n = \frac{\omega}{\omega_0}$. The magnification factor is then

$$\frac{\theta_0}{\theta_{st}} = \frac{1}{\delta} \tag{25}$$

where δ is the damping, as expressed in Equation 15.

As mentioned above, the damping is very slight in this type of system. Here, $\delta = 0.04$, i.e., $\frac{\theta_0}{\theta_{st}} \sim 25$ at resonance. When $\theta > \theta_{st}$, there is a difference in the forces of the yarn parts surrounding the pulley, due to acceleration of the pulley, which is already written in (21)

$$k(2R\theta - x) \tag{26}$$

provided that the parts are of equal length.

Due to a high amplitude magnification, the difference in force of the yarn parts can be considerable at the points of maximum acceleration of the pulley. However, the magnification is limited by the friction forces between the yarn and the pulley so that the yarn will slip against the pulley when the maximum acceleration forces have attained a critical value. When slipping occurs, equations representing sinusoidal motions are no longer valid.

The amplitude magnification for different values of n is more or less pronounced, depending on the magnitude of damping; this is shown in Figure 10. It can be seen that, when $\delta = 0$, the amplitude at resonance is infinite. Below $n = 0.5$ the magnification is, however, very low even if damping is slight.

Thus a yarn and pulley system does not amplify the amplitudes of a forced vibration, as long as the resonant frequency of the system is at least twice as high as the forced frequency. However, the magnitude of the frequency from various vibrating sources in the yarn path is usually unknown during yarn force measurement. For that reason it must be considered as doubtful whether any recorded variations with a frequency near the resonant frequency of the yarn and pulley system are true for the actual yarn process.

In connection with slipping, an apparently steady, slow rotation on the part of the pulley was observed during the experiment, according to Figure 11. When the frequency of the mechanical vibrator was slowly increased, the pulley suddenly began to rotate in one direction. Near the resonant frequency of the yarn and pulley system, the pulley ceased to rotate; above this frequency, it began to rotate in the opposite direction. This has been attributed to a dissymmetry of the maximum available friction force between yarn and pulley when maximum pulley acceleration occurs, because the vibrator acts on only one of the yarn parts and gives rise to more slipping in one direction. The change in direction has been attributed to variation in the phase angle (φ) between the motions of the vibrator and the pulley near resonance. (At resonance, $\varphi = 90°$.)

Vibrations in a System of a Transducer Pulley and a Yarn

During the measurement of yarn forces, a pulley is usually suspended from a transducer. It is there-

fore of interest to see how the transducer reacts to yarn and pulley vibrations. In Figure 12 the yarn parts have equal length. The force on the transducer (P_T) can be written

$$P_T = 2\,P_0 \pm [k(x - R\theta) + kR\theta] \qquad (27)$$

where P_0 = the yarn force at zero deflection of the vibrator spring.

Equation 27 becomes

$$P_T = 2\,P_0 \pm kx \qquad (28)$$

The maximum value of this is

$$P_T = P_0 \pm kx_{st} \qquad (29)$$

where x_{st} = the amplitude of the vibrator spring.

Thus the transducer picks up only the force induced by the "static" motion of the vibrator and not the additional forces in the yarn due to the amplitude magnification of the pulley.

If the lengths of the yarn parts are not equal (spring constants k_R and k_L in Figure 13), Equation 27 takes the form

$$P_T = 2\,P_0 \pm [k_R(x - R\theta) + k_L R\theta] \qquad (30)$$

or

$$P_T = 2P_0 \pm [k_R\,x + R\theta\,(k_L - k_R)] \qquad (31)$$

In this case the transducer will pick up some part of the additional yarn forces, the magnitude depending on the difference $k_L - k_R$.

Systems of a Stationary Yarn and More Than One Pulley

A system with two pulleys can be represented by the model in Figure 14, the two bodies (m_1, m_2) being coupled with three springs (k_1, k_2, k_3). The vibration of such a system will be composed of two main vibrations, called the first and the second main vibration.

In the first main vibration the bodies move in phase and with the same amplitude, so that no energy is expended by the center spring. The two bodies act as one with the mass $m = m_1 + m_2$; if damping is slight, the frequency can be written

$$\omega_{0I}^2 = \frac{k_1 + k_2}{m_1 + m_2} \qquad (32)$$

In the second, more rapid, main vibration, the bodies move 180° out of phase, so that one point of the center spring can be looked upon as fixed; the parts of this spring are automatically adjusted to give the same frequencies of the two body and spring systems.

The frequency is

$$\omega_{0II}^2 = \omega_{0I}^2 + \frac{4\,k_3}{m_1 + m_2} \qquad (33)$$

With different amplitudes and phase displacements with respect to each other, these main vibrations can produce innumerable types of vibrations in the system as a whole.

A system of yarn and two pulleys is shown in Figure 16. Here the first main vibration is the most important, and its frequency becomes (if damping is slight)

$$\omega_{0I}^2 = \frac{2\,(k_1 + k_2)}{m_1 + m_2} \qquad (34)$$

The interaction between the motions of the two pulleys can influence the measurement of yarn forces in various ways, which are illustrated in the following example.

Pulley *A* in Figure 16 was suspended in a transducer and pulley *C* was fixed. The yarn lengths were about 65 cm. When vibrations were induced in the system with the vibrator at slowly increasing frequencies, the yarn force vs. time diagram was recorded according to Figure 15. At low frequencies, the recorded yarn force amplitudes corresponded to the deflection of the vibrator spring, but at 40 vib./sec. the force amplitudes decreased, then rapidly increased to a maximum at 50 vib./sec. (the first main vibration). The force amplitudes obviously decreased, because the amplitude magnifications of the pulleys together with the phase angle between their motions minimized the resulting force on the transducer at 40 vib./sec.

During yarn force measurements, a three-pulley system is quite common (Figure 1). The first main vibration is developed in the same manner as described above; i.e., the resonant frequency is determined by the lengths of the yarn parts and the sum of the pulley masses. However, analogous to

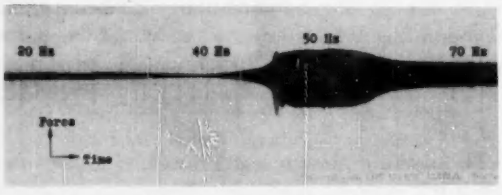

Fig. 15. Recorded yarn force amplitudes in a system of a yarn and two pulleys with an increasing frequency of the constant amplitude, sinusoidal disturbance.

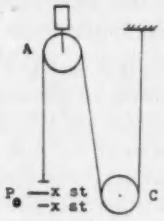

Fig. 16. System of a yarn and two pulleys.

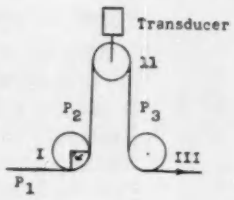

Fig. 17. Acceleration of the pulleys causes additional forces in the yarn.

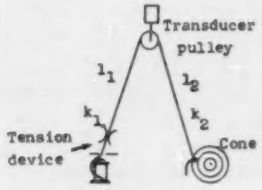

Fig. 18. Simplified cone winding arrangement.

the case of one pulley, the transducer will not feel the additional forces due to the amplitude magnification of the pulleys if the surrounding yarn parts have equal lengths.

Measurement Errors when Pulleys are Driven by a Running Yarn

Yarn Forces Needed to Accelerate a Pulley

In many yarn processes, the yarn runs at varying speeds. If a pulley is put into the yarn path, the pulley must be accelerated by the yarn, which causes additional forces in the yarn. Considering the three-pulley system in Figure 17 with the yarn speed = U, angular frequency of the pulley = ω, coefficient of friction yarn/pulley = μ, yarn forces = P_1, P_2, P_3, and the angle of contact, yarn/pulley = α, the equation of motion for the guide pulley I can be written

$$R\,(P_2 - P_1) = J\dot{\omega} \tag{35}$$

With $R\omega = U$ and $R\dot{\omega} = \dot{U}$, equation 35 becomes

$$P_2 - P_1 = \frac{J}{R^2}\dot{U} \tag{36}$$

Substituting $J = \frac{1}{2}\,m\,R^2$,

$$P_2 - P_1 = \frac{m}{2}\dot{U} \tag{37}$$

With the same mass of the transducer pulley II, this will give the same additional force[4]. Thus the total acceleration force on the transducer (ΔP_T) becomes, with $\alpha = 90°$

$$\Delta P_T = 3\frac{m}{2}\dot{U} \tag{38}$$

There is a maximum level of ΔP_T, determined by the friction between the yarn and the pulley. This can be written for pulley I

$$(P_2 - P_1)_{\max} = P_1\,(e^{\mu\alpha} - 1) \tag{39}$$

An example is chosen from a cone-winding machine, where the mean acceleration of the yarn is 20 m./sec.^{2} during the guide motion toward the bigger cone-end. The yarn force is 30 p., the mass of the three pulleys is 2 g. each, and $\alpha = 90°$.

Assuming that there is no slipping of the yarn against the pulley, we get

$$\Delta P_T = \frac{3\cdot 2}{2\cdot 981}\cdot 20\cdot 10^2 = 6.1\ p.$$

When the yarn force is 30 p., the force on the transducer is 60 p. Then the error due to the acceleration of the two pulleys is $\sim 10\%$.

Eccentricity of the Transducer Pulley

Due to imperfect balancing of a pulley, centrifugal forces are developed when the pulley is rotated. These forces act on the bearing of the pulley and hence on the transducer with the frequency

$$f = \frac{U}{2\pi R}$$

With the center of gravity lying at the distance e from the center line of the pulley, the centrifugal force on the transducer can be written

$$\Delta P = me\left(\frac{U}{R}\right)^2 \sin\left(\frac{U}{R}t\right) \tag{40}$$

Extending the above-mentioned example of cone-winding, it is assumed that the mean yarn speed (U) is 4 m./sec., e = 5/100 mm., and R = 5 mm. The maximum additional force on the transducer is then

$$P = \frac{2\cdot 5\cdot 10^{-3}}{981}\cdot\left(\frac{400}{0.5}\right)^2\cdot 1 = 6.5\ p.$$

[4] The third pulley III will also give an additional force in the yarn, but this is not felt by the transducer.

fore of interest to see how the transducer reacts to yarn and pulley vibrations. In Figure 12 the yarn parts have equal length. The force on the transducer (P_T) can be written

$$P_T = 2\,P_0 \pm [k(x - R\theta) + kR\theta] \qquad (27)$$

where P_0 = the yarn force at zero deflection of the vibrator spring.

Equation 27 becomes

$$P_T = 2\,P_0 \pm kx \qquad (28)$$

The maximum value of this is

$$P_T = P_0 \pm kx_{st} \qquad (29)$$

where x_{st} = the amplitude of the vibrator spring.

Thus the transducer picks up only the force induced by the "static" motion of the vibrator and not the additional forces in the yarn due to the amplitude magnification of the pulley.

If the lengths of the yarn parts are not equal (spring constants k_R and k_L in Figure 13), Equation 27 takes the form

$$P_T = 2\,P_0 \pm [k_R(x - R\theta) + k_L R\theta] \qquad (30)$$

or

$$P_T = 2P_0 \pm [k_R\,x + R\theta\,(k_L - k_R)] \qquad (31)$$

In this case the transducer will pick up some part of the additional yarn forces, the magnitude depending on the difference $k_L - k_R$.

Systems of a Stationary Yarn and More Than One Pulley

A system with two pulleys can be represented by the model in Figure 14, the two bodies (m_1, m_2) being coupled with three springs (k_1, k_2, k_3). The vibration of such a system will be composed of two main vibrations, called the first and the second main vibration.

In the first main vibration the bodies move in phase and with the same amplitude, so that no energy is expended by the center spring. The two bodies act as one with the mass $m = m_1 + m_2$; if damping is slight, the frequency can be written

$$\omega_{0I}^2 = \frac{k_1 + k_2}{m_1 + m_2} \qquad (32)$$

In the second, more rapid, main vibration, the bodies move 180° out of phase, so that one point of the center spring can be looked upon as fixed; the parts of this spring are automatically adjusted to give the same frequencies of the two body and spring systems.

The frequency is

$$\omega_{0II}^2 = \omega_{0I}^2 + \frac{4\,k_3}{m_1 + m_2} \qquad (33)$$

With different amplitudes and phase displacements with respect to each other, these main vibrations can produce innumerable types of vibrations in the system as a whole.

A system of yarn and two pulleys is shown in Figure 16. Here the first main vibration is the most important, and its frequency becomes (if damping is slight)

$$\omega_{0I}^2 = \frac{2\,(k_1 + k_2)}{m_1 + m_2} \qquad (34)$$

The interaction between the motions of the two pulleys can influence the measurement of yarn forces in various ways, which are illustrated in the following example.

Pulley *A* in Figure 16 was suspended in a transducer and pulley *C* was fixed. The yarn lengths were about 65 cm. When vibrations were induced in the system with the vibrator at slowly increasing frequencies, the yarn force vs. time diagram was recorded according to Figure 15. At low frequencies, the recorded yarn force amplitudes corresponded to the deflection of the vibrator spring, but at 40 vib./sec. the force amplitudes decreased, then rapidly increased to a maximum at 50 vib./sec. (the first main vibration). The force amplitudes obviously decreased, because the amplitude magnifications of the pulleys together with the phase angle between their motions minimized the resulting force on the transducer at 40 vib./sec.

During yarn force measurements, a three-pulley system is quite common (Figure 1). The first main vibration is developed in the same manner as described above; i.e., the resonant frequency is determined by the lengths of the yarn parts and the sum of the pulley masses. However, analogous to

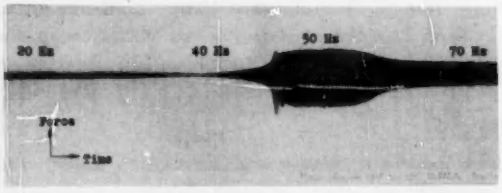

Fig. 15. Recorded yarn force amplitudes in a system of a yarn and two pulleys with an increasing frequency of the constant amplitude, sinusoidal disturbance.

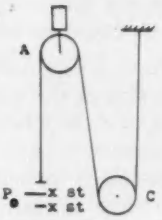

Fig. 16. System of a yarn and two pulleys.

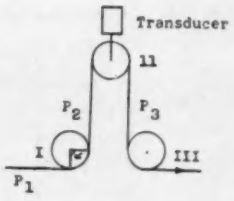

Fig. 17. Acceleration of the pulleys causes additional forces in the yarn.

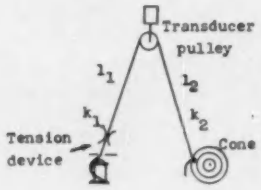

Fig. 18. Simplified cone winding arrangement.

the case of one pulley, the transducer will not feel the additional forces due to the amplitude magnification of the pulleys if the surrounding yarn parts have equal lengths.

Measurement Errors when Pulleys are Driven by a Running Yarn

Yarn Forces Needed to Accelerate a Pulley

In many yarn processes, the yarn runs at varying speeds. If a pulley is put into the yarn path, the pulley must be accelerated by the yarn, which causes additional forces in the yarn. Considering the three-pulley system in Figure 17 with the yarn speed = U, angular frequency of the pulley = ω, coefficient of friction yarn/pulley = μ, yarn forces = P_1, P_2, P_3, and the angle of contact, yarn/pulley = α, the equation of motion for the guide pulley I can be written

$$R\,(P_2 - P_1) = J\dot{\omega} \tag{35}$$

With $R\omega = U$ and $R\dot{\omega} = \dot{U}$, equation 35 becomes

$$P_2 - P_1 = \frac{J}{R^2}\dot{U} \tag{36}$$

Substituting $J = \frac{1}{2}\,m\,R^2$,

$$P_2 - P_1 = \frac{m}{2}\dot{U} \tag{37}$$

With the same mass of the transducer pulley II, this will give the same additional force[4]. Thus the total acceleration force on the transducer (ΔP_T) becomes, with $\alpha = 90°$

$$\Delta P_T = 3\frac{m}{2}\dot{U} \tag{38}$$

There is a maximum level of ΔP_T, determined by the friction between the yarn and the pulley. This can be written for pulley I

$$(P_2 - P_1)_{\max} = P_1\,(e^{\mu\alpha} - 1) \tag{39}$$

An example is chosen from a cone-winding machine, where the mean acceleration of the yarn is 20 m./sec.^{2} during the guide motion toward the bigger cone-end. The yarn force is 30 p., the mass of the three pulleys is 2 g. each, and $\alpha = 90°$.

Assuming that there is no slipping of the yarn against the pulley, we get

$$\Delta P_T = \frac{3\cdot 2}{2\cdot 981}\cdot 20\cdot 10^2 = 6.1\ p.$$

When the yarn force is 30 p., the force on the transducer is 60 p. Then the error due to the acceleration of the two pulleys is $\sim 10\%$.

Eccentricity of the Transducer Pulley

Due to imperfect balancing of a pulley, centrifugal forces are developed when the pulley is rotated. These forces act on the bearing of the pulley and hence on the transducer with the frequency

$$f = \frac{U}{2\pi R}$$

With the center of gravity lying at the distance e from the center line of the pulley, the centrifugal force on the transducer can be written

$$\Delta P = me\left(\frac{U}{R}\right)^2 \sin\left(\frac{U}{R}t\right) \tag{40}$$

Extending the above-mentioned example of cone-winding, it is assumed that the mean yarn speed (U) is 4 m./sec., e = 5/100 mm., and R = 5 mm. The maximum additional force on the transducer is then

$$P = \frac{2\cdot 5\cdot 10^{-3}}{981}\cdot\left(\frac{400}{0.5}\right)^2\cdot 1 = 6.5\ p.$$

[4] The third pulley III will also give an additional force in the yarn, but this is not felt by the transducer.

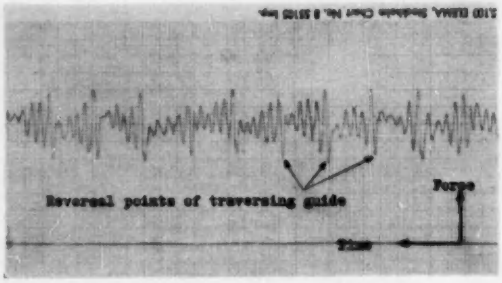

Fig. 19. Force variations in cone winding due to yarn and pulley vibrations.

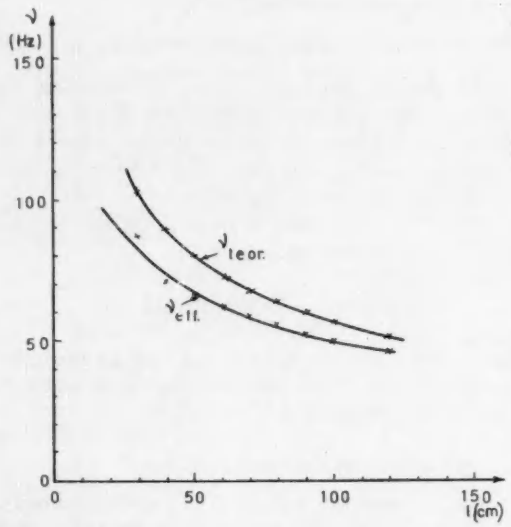

Fig. 20. Difference between calculated and theoretical value of ν, with a yarn tension device in the yarn path.

At certain speeds an eccentric pulley can also cause vibrations at resonance of the moving parts of the transducer, leading to serious errors in measurement. This will be dealt with later in this paper.

Friction in Pulley Bearings

The friction forces depend on the type of bearing used, and the calculation of the forces varies with the type. Generally it can be stated that the influence of bearing friction on the yarn forces is lessened with an increased radius of the pulley. During the measurements described in this paper, the friction forces from the ball bearings or jewel bearings have been negligible. However, when stray fibers collect in the ball bearings the friction forces are increased considerably.

Vibrations in a Yarn and Pulley System, Especially with a Yarn Tension Device in the Yarn Path

With running yarn, it is assumed that vibrations are propagated according to the same rules as with stationary yarn, and that the vibrations are superpositioned on the normal rotation of the pulleys. Vibrations can be produced by sudden changes in yarn force or speed (free vibrations) or by some vibrating body in the yarn path (forced vibrations).

In a few cases, when the yarn is rolled from one yarn package to another, the above assumptions were confirmed. However, in most processes the yarn is drawn over-end, forming a balloon; then it passes a tension device. In such cases the equations from the stationary yarn case were found not to be valid.

Figure 18 shows a simplified cone-winding arrangement, where the yarn passes only a transducer pulley A between the tension device and the traversing guide.

At the reversal points of the traversing guide the yarn speed is decreased very rapidly, which introduces free vibrations in the yarn and pulley system. The resulting yarn force variations are shown in Figure 19.

In the calculations of the resonant frequency of the system according to Figure 18, it was first assumed that the yarn parts acting as springs were l_1 and l_2, where l_1 was the part between the tension device and the pulley and l_2 the part between the pulley and the guide. The calculation was made according to

$$\omega_0^2 = \frac{2\,(k_1 + k_2)}{m} \qquad (18)$$

However, the recorded frequencies were much lower than the calculated. Further investigations showed that the yarn part l_1 had no influence on the resonant frequency; i.e., only the part l_2 was acting as a spring. Then Equation 18 could be transformed to

$$\omega_0^2 = \frac{2\,k_2}{m} \qquad (47)$$

Figure 20 shows the calculated values for different l_2 together with the recorded. However, the latter are lower, and the difference between them increases for a decreasing l_2, i.e., for higher frequencies. This might be attributed either to slipping between pulley and yarn or to forces opposed to the motion of the pulley due to the action of the tension device.

The above-mentioned example of cone-winding gives repeated free vibrations in the yarn and pulley system. A vibrating body in the yarn path induces vibrations in the system; if they are near the resonant frequency of the system, they can cause considerable force variations in the yarn. Such disturbances are often caused by vibrating machine parts or eccentric winding-up. In pirn winding, the pirn can be bent or held eccentrically in the spindle, thus giving periodical changes in yarn speed. Figure 21 (top) shows a yarn-force diagram, where the number of revolutions of the spindle is near the natural frequency of the yarn and the measuring pulley. The arrangement is equal to that of Figure 18. In Figure 21 (bottom) the number of revolutions is much lower.

Sometimes vibrations during measurements can be avoided by removing the disturbing source. If this is not possible, the resonant frequency of the yarn and pulley system can be changed by using other yarn lengths and pulley weights. Usually the frequency response of the recorder is limited; then vibrations can, in most cases, be avoided by the choice of a high natural frequency of the system compared to the frequency response of the recorder.

Transducer Vibrations

The manner of operation of a transducer is based upon spring elements, in which the moving parts are suspended. Their deflection for a certain force is usually very small, so that it does not influence the measurement of yarn forces. However, it is difficult to obtain a proper mechanical damping of very small motions, so the spring system can easily be made to vibrate. In most yarn processes there are developed force components, which will start transducer vibration. If its frequency lies within the frequency response of the recorder, the measurement can be disturbed. An example is shown in Figure 22 (top), where the yarn forces during weaving are measured with a Statham strain gauge (natural frequency with pulley = 200 vib./sec.) and recorded with the Elema recorder. In Figure 22 (bottom), the same apparatus is used, though with an electrical filter, which lets through only frequencies of up to 100 vib./sec. The Brush and the Kelvin Hughes recorders have given curves corresponding to that in Figure 22 (bottom). Thus the disturbing frequencies from the vibrating transducer may be cut either electrically through a filter or mechanically through a recorder with a suitable frequency response.

However, even if a filter or an appropriate recorder is used, transducer vibrations can cause disturbances in some special cases when the yarn speed is constant. Due to small unbalances in the pulley, the moving parts of the transducer are forced to

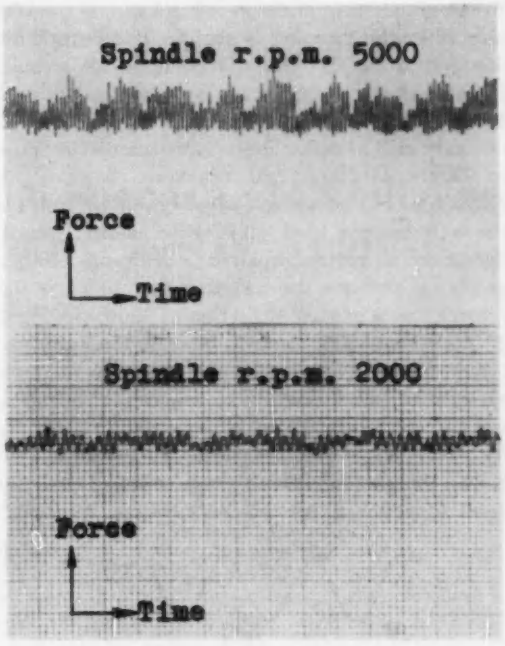

Fig. 21. Yarn force diagrams from pirn winding.

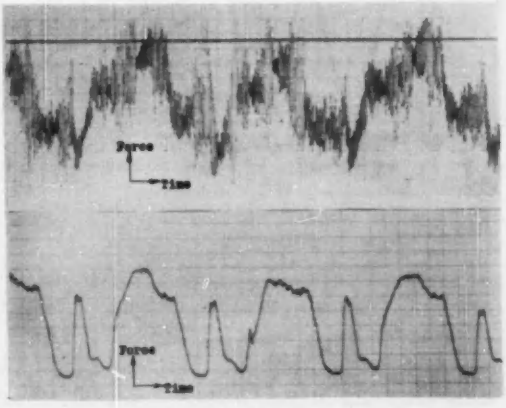

Fig. 22. Yarn force diagrams from weaving. Resonant frequency of transducer filtered in Figure 22 (bottom).

vibrate at a frequency which is equal to the number of revolutions per second of the pulley. If this number is $n\nu_0$, where ν_0 is the natural frequency of the transducer, vibrations at resonance occur for $n = 1$. However, such vibrations can also occur for $n = \frac{1}{2}, \frac{1}{3}, \frac{1}{4} \ldots$, which indicates that harmonic components are induced by the pulley—probably by vibrations in bearings. As is shown in Figure 10, the amplitude magnification at resonance is considerable when the damping is slight. The disturbances are due to the fact that a transducer for technical reasons usually is electrically null balanced near the point of rest of its unloaded spring system. An ordinary rate of deflection is then recorded as shown in Figure 23 (top). At resonance, however, the amplitudes of the spring system can be so high that the null balance level (NBL) is passed; i.e., the deflection is partly negative. With an ordinary amplitude detector the corresponding signal is then recorded as a positive deflection as shown in Figure 23 (bottom). This tends to increase the mean yarn force. Figure 24 shows an example from the measurement of shuttle yarn force, where the yarn speed was slowly increased. A three-pulley system was used together with a Statham strain gauge and the Kelvin Hughes recorder. At a critical yarn speed (and thus pulley speed), an apparent increase in yarn tension occurred, and it remained stable as long as the speed was constant. The resonant frequency of the transducer was far above the frequency response of the recorder, so the high amplitudes were not recorded.

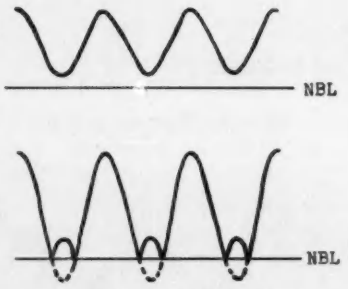

Fig. 23. Recorded sinusoidal deflection of a transducer: top, normally; bottom, at resonance.

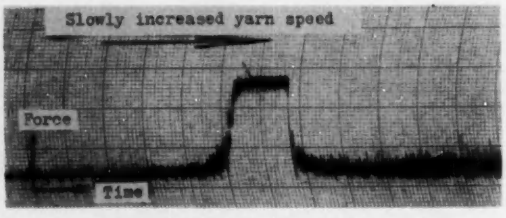

Fig. 24. Measurement of shuttle yarn force, with slowly increased yarn speed.

As a secondary complication of the vibrations described, the vacuum tube of the last amplifier stage can be overloaded, giving a high DC-signal that is recorded as a marked increase in yarn force.

An adequate damping of the transducer seems to be the best way to overcome disturbances. They can also be eliminated electrically by using a phase detector instead of an amplitude detector in the electric circuit.

In many processes, the yarn speed varies, and during force measurement the yarn (and pulley) speed can attain critical values for a short time. This has been found not to influence the measurement.

Conclusions

The measurement of yarn tensile forces is made either to control or to adjust the forces or to investigate the effect on these forces from the different process stages. The use of pulleys in the measuring unit can produce disturbances because the yarn and the pulleys form vibrating systems with rather low natural frequencies and slight damping, so that vibrations are easily developed. Furthermore, shortcomings of the mechanical and electrical part of the measuring equipment can cause errors during measurement. The different kinds of errors can be summarized:

1. The amplitudes of original force variations are magnified; this may or not be picked up by the measuring device.
2. Force variations are sometimes recorded which are not to be found in the yarn.
3. The recording system is unable to discern force variations in the yarn.
4. The yarn force level is increased; this may be wholly or partly recorded.
5. A higher force level is recorded which does not originate from the yarn.

Many of these disturbances occur only in special cases; e.g., with stationary yarn or at certain constant yarn speeds etc.

Yet these problems might give enough reason to consider a replacement of the pulleys by nonrotating

elements. This would, however, mean that frictional forces must be considered, and such forces depend on yarn speed, surface qualities of yarn and guides, and other things. Furthermore, pulleys are used in most commercial measurement devices. The main thing is therefore to get a good knowledge of the various pulley problems, including such factors as the frequency response of the recorder, the resonant frequency of the transducer, and the data of the pulleys. Furthermore, it is recommendable to observe yarn speed, yarn length adjacent to the pulley, and spring constant of the yarn in the process in question.

Literature Cited

1. Barach, J. L., TEXTILE RESEARCH JOURNAL **19**, 355 (1949).

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On the Size of the Intermicellar Spaces and Capillaries in Jute Fibers as Revealed by X-Ray Analysis

S. K. Chowdhury

Technological Research Laboratories, Indian Central Jute Committee, Calcutta, India

Abstract

The dimensions of the intermicellar regions and capillaries in raw jute fibers have been estimated from the sizes of the colloidal gold and silver particles deposited in the fiber under different conditions of deposition. It has been inferred that the dimensions of the colloidal particles indicate only the dimensions of the capillaries after they have been enlarged by swelling or by the deposition process itself. The size of the particles determined is of the order of 100 Å in raw jute fiber; it has been pointed out that they remain within wider capillaries present in jute fiber because the intermicellar region is too small to accommodate these particles. Unlike ramie, in jute fibers treated for a short time with weaker solutions these particles cannot form even within these capillaries. They form within much wider capillaries (about 200 Å in diameter), partly because the smaller capillaries are blocked by the noncellulosic amorphous materials (especially lignin) and partly because the swelling of ramie fibers is faster than that of jute fibers having a very high lignin content. This has also been corroborated by the fact that the dimensions of these dispersoids in holocellulose increase to 126 Å.

IT IS well known that in all native fibers the micellar structure is interspersed with fine capillaries, which are distributed irregularly in the structure of the fiber. These capillaries are too small to be observed under a powerful microscope. Frey-Wyssling [6] investigated the size of these capillaries by depositing colloidal particles inside them and estimating the size of the particles from the half intensity width of the Debye-Scherrer rings given by the particles. He observed that the size of such colloidal particles of gold formed inside silk and wool is about 50 Å; in ramie it is 100 Å. The size, however, depended on the speed at which the particles were developed in the capillary system. He concluded from these results that in ramie fibers there must be two categories of submicroscopic spaces—(1) narrow intermicellar spaces, of the order of magnitude 10 Å, which are responsible for the phenomenon of swelling, and (2) wider capillary spaces which are accessible to dyes of much higher dimensions and to the hardening substances—lignin, cutin, etc. Heyn [8] investigated the deposition of gold particles into spaces between micelles by studying the small angle scattering by jute fiber incrusted

TABLE I. Samples Studied by X-Rays with the Details of Treatment

Sample	Solution	Time treated and reduced
Ia. Raw jute fiber	2% gold chloride	3 hr.
b. Raw jute fiber	2% gold chloride	40 hr.
c. Raw jute fiber	6% gold chloride	40 hr.
d. Raw jute fiber	2% silver nitrate	40 hr.
e. Raw jute fiber	7.5% silver nitrate	40 hr.
IIa. Holocellulose	2% gold chloride	40 hr.
IIIa. Alphacellulose	2% gold chloride	40 hr.
b. Alphacellulose	2% silver nitrate	40 hr.
c. Alphacellulose	7.5% silver nitrate	40 hr.
IV. Raw jute fibers washed with water and alcohol-benzene (1:1).		
V. Raw jute fibers treated with 2%, 6% gold chloride solution and 7.5% silver nitrate solution for 40 hr. but not reduced.		

with colloidal gold particles and comparing with the small angle scattering due to the raw jute fibers. He concluded that the gold particles fill only part of the intermicellar crevices.

More recently Heyn [11] has investigated the radial distribution of micelles in jute from the small angle scattering in the dry condition and in the water-swollen stage. He has concluded from the results obtained that in the dry jute fiber the average distance between the micelles is 35 Å, while in the water-swollen fiber it is 53 Å. Banerjee and Chakraburtty [1] incrusted a number of fibers including raw jute with colloidal gold and colloidal silver. They observed that the size of the dispersoids was 80–84 Å in the case of raw jute fiber and concluded that the dimensions of the intermicellar spaces are given by this particle size.

It has been suggested by previous workers [8] that the deposition of particles occurs mainly in the swollen fiber and the growth of the incrusted particles might force the micelles still further apart during the process of deposition ("dry swelling" [8]). The present paper intends to bring a further analysis of this question and also considers to what extent these dimensions of the intermicellar spaces and capillaries depend on the removal of lignin and hemicelluloses from jute fibers. For this purpose the size of the gold and silver particles formed was studied in raw jute fiber, and in holocellulose and alphacellulose from jute fiber, under different conditions of particle deposition.

Experimental

Good quality Tossa Jute (*Corchorus olitorius*) was selected for the investigation. A quantity of the fiber was washed in water to remove impurities and dried in air. Fats and waxes etc. were extracted with a 1:1 mixture of alcohol and benzene in the Soxhlet apparatus. Holocellulose and alphacellulose from the same sample of jute fiber were prepared according to the method of Sarkar, Mazumder, and Pal [11]. Holocellulose prepared by this method is completely free from lignin and partly free from hemicelluloses, whereas alphacellulose is free from all other noncellulosic constituents. Following Ambronn, these fibers were treated with solutions of silver nitrate (2–7.5% by weight) and gold chloride (2–6% by weight) at room temperature (30–35° C.) for several hours. The treatment was carried out in the dark to prevent premature reduction of the metals. The fibers were taken from the solutions and rinsed with distilled water, then carefully dried with filter paper. Finally, according to Frey [5], the solution was reduced by hydrazin hydrate. With all the samples, the process of reduction was carried out very slowly and gently.

The treatments to which the samples were subjected are given in Table I.

Sample V was studied because jute fiber contains reducing groups which may cause premature reduction of the gold and silver metals in the fiber. An X-ray diffraction photograph of gold wire of the same dimensions of the sample was taken to determine and correct for the geometrical broadening produced by the camera when used to determine the half-widths of the Debye-Scherrer rings.

X-ray diffraction photographs of intensities suitable for photometry were taken using bundles of fibers containing 12–15 filaments, combed to ensure parallelism. In the case of holocellulose, the fibers were made parallel with extreme difficulty; the parallelism was not perfect. Alphacellulose was practically in the form of a powder. The camera used was a cylindrical one with radius 2.86 cm. CuK radiation filtered through nickel foil from a Hadding X-ray tube was used. The specimen size, exposure time, and photographic technique were maintained uniform for all the samples as far as practicable. The tube was run at 45 KV., 5 mA.

Microphotometric records were taken with a Moll type self-recording microphotometer; on each record the deflections corresponding to the infinite density

and the unexposed portion of the film were recorded. The intensity at any point in the spot was determined by first determining the total intensity at that point and then subtracting from it the intensity of the background with respect to the unexposed portion of the film. Care was taken to allow the spot of light focused on the film to move along the equatorial direction. It was also necessary to draw a log intensity density curve. This was done by the method explained earlier by Chowdhury and Sirkar [3].

The sizes of the gold and silver particles were calculated by the usual method [15] from the width of the interference rings of gold and silver at the positions having intensities equal to half that at maximum, taking into account the magnification of the microphotometer. The general equation used to determine the particle size is

$$B \cos \frac{\chi_m}{2} = 0.9\lambda \left[\frac{\frac{h^2}{m_1^2 a^4} + \frac{k^2}{m_2^2 b^4} + \frac{l^2}{m_3^2 c^4}}{\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}} \right]^{\frac{1}{4}}$$

where B is the half intensity width of the hkl reflection in radians, which is equal to the width mentioned above, χ_m is the angle between the incident and reflected X-rays, and m_1, m_2, and m_3 denote the number of times the unit cell is repeated along a, b, and c axes respectively. The values of m which denote the number of times the unit cell of gold and silver particles is repeated in different directions were obtained from Laue's [12] formula, used for rhombic lattices.

In the case of gold, if B represents the half-width of the 002 ring, the above formulae reduces to

$$m = \frac{.3679}{B}$$

By multiplying these observed values of m with the axial length, the average dimension of the colloidal particles was determined in all the cases. The axial lengths for gold and silver crystals were taken as $a_{Au} = 4.07042$ Å and $a_{Ag} = 4.07787$ Å. The broadening B may be to some extent due to width of the incident beam and the sample; this was eliminated by the method adopted by Chowdhury [2] from the measured half-width of the lines of gold wire of the same size as that of the irradiated sample under identical conditions in the same camera.

The photographs of the patterns are reproduced in Figures 1 and 2; the results obtained are shown in Table II.

Results and Discussion

It is seen from Table II that a large space is occupied by these crystalloids. The width of the micelles of jute fiber as determined by Chowdhury and Sirkar [3] from line-broadening of the X-ray diffraction pattern is of the order of 50 Å, and that obtained by Heyn [9, 10] from small angle scattering data is of the order of 28 Å. Taking approximately 53 Å as the center-to-center distance of micelles even in the swollen state as determined more recently by Heyn [11] from small angle scattering data, it can be inferred that the micelles of jute fiber are very closely packed. Therefore the space between the micelles is too small to accommodate particles of the order of 100 Å. These particles are formed, therefore, within regions of width greater than 100 Å. These results support the view expressed by Frey-Wyssling [7] in the case of ramie fibers that the colloidal particles cannot enter the regions between micelles arranged parallel to each other. They remain within wider capillaries present in the jute fiber.

It can be seen from Table II that with milder treatments of jute fibers with 2% gold chloride for 3 hr. followed by reduction, the particles embedded are much larger than those formed in the case of longer treatment. During short treatment with weak solution, the solution enters only the wider capillaries or bigger crevices and cracks. On the other hand, in the case of ramie (a comparatively pure cellulosic fiber) treated with only 1–2% gold chloride solution for periods as short as 2–3 hr. and reduced by hydrazin hydrate, the particles are formed within capillaries of width about 100 Å. This difference may be due partly to the fact that passages leading to these capillaries within jute fibers are partially blocked by noncellulosic amorphous materials, especially lignin, while these are free in ramie. This

TABLE II. Size of the Embedded Particles in Different Samples due to Different Treatments

Samples	Metal embedded	% of metal solution used	Time of treatment, hr.	Calculated particle size, Å
Raw jute	gold	2	3	199
Raw jute	gold	2	40	102
Raw jute	gold	6	40	102
Holocellulose	gold	2	40	126
Raw jute	silver	2	40	89
Raw jute	silver	7.5	40	89

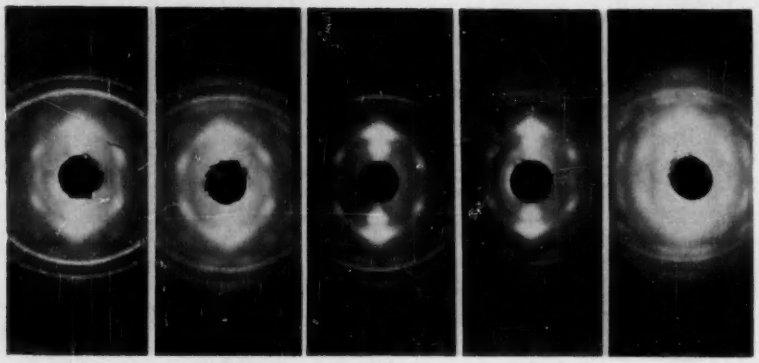

Fig. 1. X-ray diffraction patterns of jute fibers (A) treated with 6% gold chloride solution (40 hr.) and reduced, (B) treated with 2% gold chloride solution (40 hr.) and reduced, (C) treated with 2% gold chloride solution (3 hr.) and reduced, (D) treated with 2% silver nitrate solution (40 hr.) and reduced, and (E) treated with 7.5% silver nitrate solution (40 hr.) and reduced.

difference may also indicate that swelling of the fiber as observed through a microscope by Sen and Hermans [14] widens the capillaries; this is effected more quickly in ramie, owing to absence of lignin. Hence it is to be inferred that the dimensions of the colloidal particles indicate only the dimensions of capillaries after they have been enlarged by swelling. The very fact that when all the lignin is removed from jute fiber holocellulose is formed and the dimensions of the dispersoids in holocellulose increase to 126 Å corroborates this view, because swelling of holocellulose is more than that of raw jute. It should also be noted that when the fibers are treated for a long time with the solution of gold chloride or silver nitrate, then rinsed with distilled water and dried with filter paper, the fibers are not in a fully swollen state, but rather are semi-swollen. There is also a possibility of growth of incrusted crystallites inside crevices so as to force micelles apart when incrustation proceeds. By this method we cannot get any exact idea about the dimensions of the actual cavities present inside the fiber in its dry conditions.

When raw jute fibers are treated with a concentration of gold chloride solution of 6% for a period of about 40 hr. and then reduced, it can be seen from Table II that the dimensions of the particles formed are of the order of 102 Å. From the diffraction photograph (Figure 1) it can be seen that a number of spots due to colloidal gold particles lie on the Debye-Scherrer rings, indicating the presence of small single crystals of gold at random orientation. These may be formed in the intercellular regions and in very wide cavities, which become wider due to swelling. The same result is also observed when jute fibers are treated with 2% gold chloride solution for a longer period, but in this case the number of spots and their intensities are smaller.

The dimension of the colloidal particles of silver with which raw jute fiber is incrusted as given in Table II is of the order of 90 Å. From the photographs in Figure 1 it is seen that even for higher concentration of $AgNO_3$ solution and for a longer period of treatment there is no indication of the presence of single crystals of silver. This difference in behavior between the silver and gold dispersoids may be due to the difference in the formation of gold and silver crystals in the reduced solutions. It is well known that when colloidal gold particles are formed they become larger if the reaction is continued for a longer time. The speed of the reactions depends on the reducing agent (Ephraim [4]). A rise in temperature or concentration has the same effect. It hinders the formation of the nuclei, but facilitates their growth.

In the case of alphacellulose from jute fibers, it is extremely difficult under the present experimental conditions to find out the dimensions of the embedded gold and silver particles. Because in this case all irregular cavities are removed and swelling is less than that in raw jute fiber, the intensity of the lines due to gold and silver particles is weaker. Moreover, they are crowded with the diffraction rings of alphacellulose, which gives a typical powder diagram of Cellulose II. The background intensity is also too high to give any measurable peak over the background in the microphotometric record. This may be due to the fact that gold and silver particles of very small dimensions are distributed throughout the fiber, and X-rays scattered due to these minute dispersoids will resemble the pattern due to gaseous

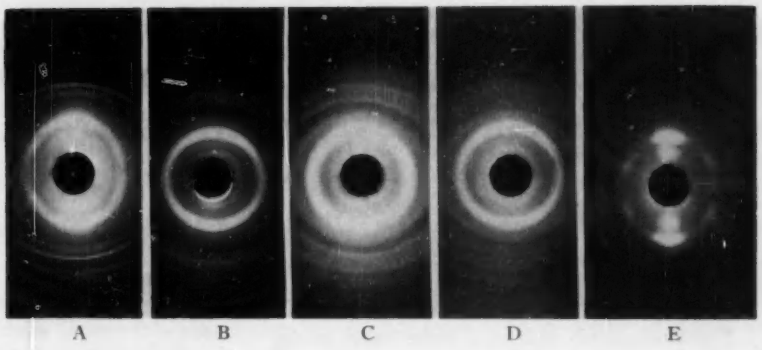

Fig. 2. X-ray diffraction patterns of (A) holocellulose treated with 2% gold chloride solution, (B) alphacellulose treated with 2% silver nitrate solution, (C) alphacellulose treated with gold chloride solution, (D) alphacellulose treated with 7.5% silver nitrate solution, and (E) jute fibers treated with 6% gold chloride solution. All were treated for 40 hr. and all but (E) were reduced.

scattering, which is diffused, contributing to the background intensity only. As all the hemicelluloses and lignin have been removed from jute fiber to form alphacellulose, the different cells which are bound together by these substances in jute fiber with capillaries in the intercellular space may be separated from each other, so that most of the capillaries disappear. The fact that not many large gold particles are deposited in alphacellulose actually leads to this conclusion and supports the conclusion that in jute fiber the big particles are formed in such large capillaries.

It has also been found that the reducing groups present in jute fibers do not cause any premature reduction of the metals to be detected by X-rays. The X-ray diagram is exactly the same as that of the jute diagram (Figure 2E).

Acknowledgments

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Literature Cited

1. Banerjee, B. K. and Chakraburtty, D. M., *Proc. Nat. Inst. Sci. (India)* **21**, 15 (1955).
2. Chowdhury, S. K., *Science & Culture* **21**, 334 (1955).
3. Chowdhury, S. K. and Sirkar, S. C., *Ind. J. Phys.* **22**, 39 (1948).
4. Ephraim, F., *Inorganic Chemistry*, p. 110 (1954).
5. Frey, A., *Z. Wiss. Mikr.* **42**, 421 (1925).
6. Frey-Wyssling, A., *Protoplasma* **27**, 372 (1937).
7. Frey-Wyssling, A., *Sub-Microscopic Morphology of Protoplasma*, Elsevier, New York, p. 101 (1953).
8. Heyn, A. N. J., TEXTILE RESEARCH JOURNAL **19**, 163 (1949).
9. Heyn, A. N. J., *J. Am. Chem. Soc.* **72**, 5768 (1950).
10. Heyn, A. N. J., *J. Appl. Phys.* **26**, 519 (1955).
11. Heyn, A. N. J., *J. Appl. Phys.* **26**, 1113 (1955).
12. Laue, M. V., *Z. Krist.* **64**, 115 (1926).
13. Sarkar, P. B., Mazumder, A. K., and Pal, K. B., *J. Textile Inst.* **39**, T44 (1948).
14. Sen, M. K. and Hermans, P. H., *Rec. trav chim. Pays Bas.* **68**, 1079 (1949).
15. Sproull, W. T., *X-Rays in Practice*, McGraw-Hill, New York, p. 446–47 (1946).

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Thermodynamic Relations Among Stresses, Deformations, and Moisture Absorption

J. W. S. Hearle

College of Technology, University of Manchester, Manchester, England

Introduction

Thermodynamic relations have been useful in various branches of engineering; therefore, it seems worth considering whether they can be applied to textile problems. A particular limitation which must always be remembered is that thermodynamic equations (as distinct from inequalities) apply only to reversible changes. They break down when there is any hysteresis and when nonequilibrium states are involved. This is a serious difficulty for textile applications, since hysteresis is a common phenomenon, but it may be possible (provided the limitation is borne in mind in any application) to use the relations, at least to get approximate results.

Generalizing Porter's [4] osmotic pressure equation, Barkas [1] has used a suitable thermodynamic cycle to obtain a differential equation relating the directional swelling of a gel to the directional stresses and the moisture absorption at constant temperature. Warburton [7] and Gurney [2] have derived similar equations from considerations of free energy. Treloar [5,6] has applied these results to fibers.

Derivation of the General Equation

The general equation depends on the number of types of deformation and stress which can occur. The derivation given here refers to a rectangular parallelepiped, subject to stresses normal to its faces and swelling in directions parallel to its sides. It is, however, easy to modify the equation for other shapes, or to add terms corresponding to other types of stress and deformation, such as shear stresses and strains.

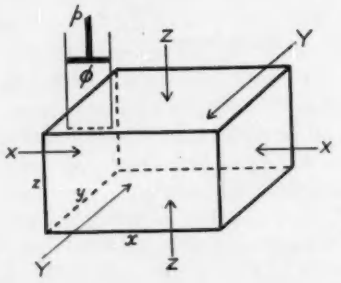

Fig. 1. Forces acting upon a specimin (parallelepiped).

We take a specimen, Figure 1, of mass m (when dry); of volume mV (i.e., V is the volume of a specimen of unit mass when dry); with sides x, y, and z; at a fractional regain r (i.e., containing a mass mr of water); and having (compressive) stresses X, Y, and Z, normal to its faces. This is in equilibrium with a container of volume ϕ containing a mass μ of vapor at a vapor pressure p. Let the specific volume of the vapor be v. It is assumed that the specimen can gain or lose water only to the vapor in the container.

We consider an isothermal change in condition of this specimen, in which the stresses change from X to $X + dX$, Y to $Y + dY$, and Z to $Z + dZ$; the lengths of the sides change from x to $x + dx$, y to $y + dy$, and z to $z + dz$; the regain changes from r to $r + dr$; and the vapor pressure changes from p to $p + dp$. The mass of vapor in the container will change from μ to $\mu - mdr$.

An isothermal cycle, shown in Figure 2 for the x-direction and for the vapor, is taken through these points as follows:

$a \rightarrow b$ Increase in vapor pressure from p to $p + dp$ at constant applied stress. Specimen absorbing moisture from container.

$b \rightarrow c$ Increase in applied stress by dX, dY, and dZ at constant vapor pressure. Moisture evaporating into container.

$c \rightarrow d$ Decrease in vapor pressure to p at constant applied stress. Moisture evaporating.

$d \rightarrow a$ Decrease in stress to X, Y, and Z. Moisture being absorbed.

As this is a reversible isothermal cycle, it follows that the total work done is zero.

(1) By force on the X-face:

$$\begin{aligned}\text{work} &= \oint (\text{force} \times \text{displacement}) \\ &= \text{area of } X\text{-face} \times (\text{area enclosed by } X, x \text{ cycle}) \\ &= \frac{mV}{x}\left(\frac{\partial x}{\partial p}\right)_{XYZ} dp.dX \end{aligned} \tag{1}$$

(2) Similarly for the Y- and Z-faces

(3) By force on vapor container:

$$\begin{aligned}\text{work} &= \oint \text{pressure} \times \text{volume} \\ &= -\ (\text{area of } p, \phi \text{ cycle})^1\end{aligned}$$

$$\text{Area of } p, \phi \text{ cycle} = dp\ (\text{increase in } \phi \text{ from } a \text{ to } d)$$

The latter term may be expressed in two ways:

(a) $$\begin{aligned}\text{increase in } \phi_{a\to d} &= \text{increase in mass of vapor in container} \times \text{specific volume of vapor} \\ &= -\ \text{increase in mass of water in material} \times \text{specific volume of vapor} \\ &= -\ m\left[\left(\frac{\partial r}{\partial X}\right)_{pYZ} dX + \left(\frac{\partial r}{\partial Y}\right)_{pZX} dY + \left(\frac{\partial r}{\partial Z}\right)_{pXY} dZ\right]v\end{aligned}$$

or

(b) $$\begin{aligned}\text{increase in } \phi_{a\to d} &= \text{increase in } \phi_{c\to e} - \text{increase in } \phi_{c\to f} \\ &= -\ mv\ (\text{increase in regain}_{c\to d} - \text{increase in regain}_{c\to a}) \\ &= -\ mv\left[\left(\frac{\partial r}{\partial p}\right)_{XYZ}(-\,dp) - (-\,dr)\right]\end{aligned}$$

$$\text{Therefore work} = m\left[\left(\frac{\partial r}{\partial X}\right)_{pYZ} dX + \left(\frac{\partial r}{\partial Y}\right)_{pZX} dY + \left(\frac{\partial r}{\partial Z}\right)_{pXY} dZ\right]vdp \tag{2a}$$

$$\text{or work} = -\ m\left[\left(\frac{\partial r}{\partial p}\right)_{XYZ} dp - dr\right]vdp \tag{2b}$$

Summing the work done, and equating to zero, we then have from Equations 1 and 2a, cancelling m and dp throughout:

$$\frac{V}{x}\left(\frac{\partial x}{\partial p}\right)_{XYZ} dX + \frac{V}{y}\left(\frac{\partial y}{\partial p}\right)_{XYZ} dY + \frac{V}{z}\left(\frac{\partial z}{\partial p}\right)_{XYZ} dZ + \left[\left(\frac{\partial r}{\partial X}\right)_{pYZ} dX + \left(\frac{\partial r}{\partial Y}\right)_{pZX} dY + \left(\frac{\partial r}{\partial Z}\right)_{pXY} dZ\right]v = 0 \tag{3}$$

Collecting coefficients, we get a series of useful relations:

$$\frac{V}{x}\left(\frac{\partial x}{\partial p}\right)_{XYZ} = -\ v\left(\frac{\partial r}{\partial X}\right)_{pYZ} \tag{4}$$

and similarly for the other two directions.

Alternatively, from Equations 1 and 2b, we have:

$$\frac{V}{x}\left(\frac{\partial x}{\partial p}\right)_{XYZ} dX + \frac{V}{y}\left(\frac{\partial y}{\partial p}\right)_{XYZ} dY + \frac{V}{z}\left(\frac{\partial z}{\partial p}\right)_{XYZ} dZ = v\left(\frac{\partial r}{\partial p}\right)_{XYZ} dp - vdr \tag{5}$$

and, multiplying through by $(\partial p/\partial r)_{XYZ}$:

$$\frac{V}{x}\left(\frac{\partial x}{\partial r}\right)_{XYZ} dX + \frac{V}{y}\left(\frac{\partial y}{\partial r}\right)_{XYZ} dY + \frac{V}{z}\left(\frac{\partial z}{\partial r}\right)_{XYZ} dZ = vdp - v\left(\frac{\partial p}{\partial r}\right)_{XYZ} dr \tag{6}$$

[1] The negative sign is introduced because the area is enclosed in the reverse direction to that of the stress cycles.

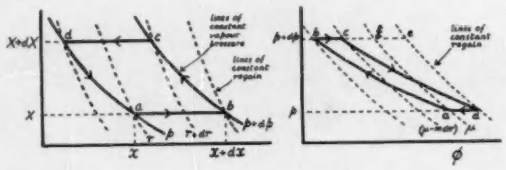

Fig. 2. Isothermal cycle for the x-direction and the vapor.

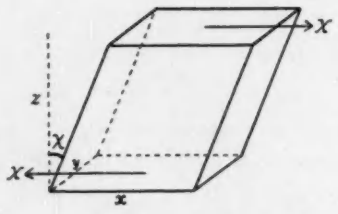

Fig. 3. Shear stress acting on the xy face in the direction x.

Equations 5 and 6 are alternative forms of the equation of state of the material for isothermal conditions.

Another form of the equation involving dx, dy, and dz instead of dr can be obtained by splitting up the expressions for the work done by the loads on each face into two terms, similar to the divisio of the work done on the vapor in (3)(b). The general expression is, however, too complicated to be useful, being of the second order in dX, dY, dZ, dx, dy, dz, and dp; the simpler forms for special cases can be derived from the relations already given.

Modification of General Equation

If the shape of the specimen is different, or if other forces are involved, the equations must be modified by the inclusion of the appropriate work terms. For example suppose, as in Figure 3, a shear stress X acts on the xy face in the direction x, giving an angle of shear, χ. Let the change in X be dX. In evaluating the work done one must add (in Equations 3 and 5) a term for the work done by the shear force:

work done by shear force

$$= \frac{mV}{z} z \left(\frac{\partial \chi}{\partial p}\right)_{XYZ_X} dp.d\mathrm{X}$$

$$= mV \left(\frac{\partial \chi}{\partial p}\right)_{XYZ_X} dp.d\mathrm{X} \quad (7)$$

To Equation 2a, one must add the term

$$m \left(\frac{\partial r}{\partial \mathrm{X}}\right)_{XYZ_p} d\mathrm{X}.vdp$$

This give a relation corresponding to Equation 4:

$$V \left(\frac{\partial \chi}{\partial p}\right)_{XYZ_X} = v \left(\frac{\partial r}{\partial \mathrm{X}}\right)_{XYZ_p} \quad (8)$$

Equation 2b is unaltered, except for the addition of **X** to the suffixes; therefore Equation 5 is changed only by the addition of $V(\partial\chi/\partial p)_{XYZ_X}d\mathrm{X}$ to the left-hand side. Equation 6 is similarly modified by the addition of $V(\partial\chi/\partial r)_{XYZ_X}.d\mathrm{X}$.

Shear forces acting on the other faces could be treated similarly.

Application to Textiles

Fibers

The equations must be modified to suit the shape of fibers. We assume that we are dealing with a cylindrical fiber of irregular cross section (Figure 4)

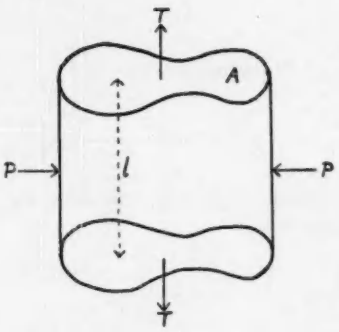

Fig. 4. Cylindrical fiber of irregular cross section.

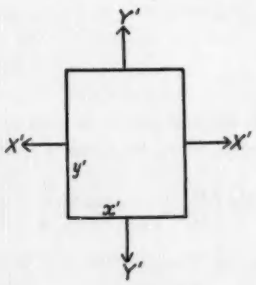

Fig. 5. Stresses in a fabric.

[2] As this is a tension, it will have the opposite sign to the forces so far considered.

with area A and length l. The forces on the fiber are a tensile stress[2] T and a uniform transverse pressure P. Under these conditions, Equation 3 becomes:

$$\frac{V}{l}\left(\frac{\partial l}{\partial p}\right)_{TP}(-dT)+\frac{V}{A}\left(\frac{\partial A}{\partial p}\right)_{TP}dP = -\left[\left(\frac{\partial r}{\partial T}\right)_{pP}dT+\left(\frac{\partial r}{\partial P}\right)_{pT}dP\right]v \quad (9)$$

This, with the similar modifications of Equation 5, leads to the equations given in Table I. It may be noted that the special case of a fiber under constant uniform transverse stress, e.g., a single fiber in air, is given by putting $dP = 0$ in these equations. More complicated directional transverse stresses would give rise to more complicated expressions, as the appropriate work terms were included in the equations.

Yarns

Yarns are geometrically similar to fibers; thus the same equations will apply.

TABLE I. Summary of Equations

Fibers and yarns:
(under uniform transverse pressure)

$$\frac{1}{l}\left(\frac{\partial l}{\partial p}\right)_{TP}=\frac{v}{V}\left(\frac{\partial r}{\partial T}\right)_{pP} \quad (10)$$

$$\frac{1}{A}\left(\frac{\partial A}{\partial p}\right)_{TP}=-\frac{v}{V}\left(\frac{\partial r}{\partial P}\right)_{pT} \quad (11)$$

$$-\frac{1}{l}\left(\frac{\partial l}{\partial p}\right)_{TP}dT+\frac{1}{A}\left(\frac{\partial A}{\partial p}\right)_{TP}dP=\frac{v}{V}\left\{\left(\frac{\partial r}{\partial p}\right)_{TP}dp-dr\right\} \quad (12)$$

$$-\frac{1}{l}\left(\frac{\partial l}{\partial r}\right)_{TP}dT+\frac{1}{A}\left(\frac{\partial A}{\partial r}\right)_{TP}dP=\frac{v}{V}\left\{dp-\left(\frac{\partial p}{\partial r}\right)_{TP}dr\right\} \quad (13)$$

Fabrics:

$$\frac{A'}{x'}\left(\frac{\partial x'}{\partial p}\right)_{X'Y'}=v\left(\frac{\partial r}{\partial X'}\right)_{pY'} \quad (14)$$

$$\frac{A'}{y'}\left(\frac{\partial y'}{\partial p}\right)_{X'Y'}=v\left(\frac{\partial r}{\partial Y'}\right)_{pX'} \quad (15)$$

$$\frac{A'}{x'}\left(\frac{\partial x'}{\partial p}\right)_{X'Y'}dX'+\frac{A'}{y'}\left(\frac{\partial y'}{\partial p}\right)_{X'Y'}dY'=-v\left(\frac{\partial r}{\partial p}\right)_{X'Y'}dp+vdr \quad (16)$$

$$\frac{A'}{x'}\left(\frac{\partial x'}{\partial r}\right)_{X'Y'}dX'+\frac{A'}{y'}\left(\frac{\partial y'}{\partial r}\right)_{X'Y'}dY'=-vdp+v\left(\frac{\partial p}{\partial r}\right)_{X'Y'}dr \quad (17)$$

where

p = vapor pressure
v = specific volume of water vapor
V = volume of specimen of unit mass when dry*
l = length
T = tensile stress
r = regain (as a fraction)
A = area of cross section
P = uniform transverse pressure

} for fiber or yarn

A' = area of unit mass (when dry)
x', y' = lengths of sides
X', Y' = force per unit length on sides (as tensions, parallel to sides x' and y')

} for fabric

* This volume should be based on the same definition of area of cross section as is used in working out the stresses T and P.

Fabrics

In fabrics one is concerned with a two-dimensional structure (Figure 5), and may usually take the stresses acting normal to the surface as constant.

Let X' and Y' be the tensile forces per unit length acting parallel to the sides, of length x' and y' respectively, of a piece of fabric, with A' as the area of unit mass. Modification of the general equations then gives the equations for fabrics in Table I.

Possible Uses of These Equations

Table I summarizes the equations for fibers, yarns, and fabrics. In practical application two points must be borne in mind. First, the equations, being thermodynamic relations, apply exactly only to reversible changes. They can take no account of hysteresis in moisture absorption, of nonrecoverable deformations, or of relaxation of stress. Second, the results are all given as differential equations. Direct integration is not possible, since the quantities vary with one another in ways which have not been analytically expressed. For example, the specific volume of water vapor v varies with the vapor pressure p; the volume of fiber V, the area of fabric A', and the various differential coefficients will vary somewhat with the regain and stresses in the material. Exact integration would be possible numerically, but would involve considerable computation. However, approximate results, which may be useful, can be obtained by assuming the above quantities constant or by applying approximate corrections.

The equations may be used to extend the applications of limited experimental results. Applied to data which is available or easily measured, it can give information which would be difficult or more troublesome to obtain by direct experiment.

Equation 10 relates the change of length of fibers or yarns with vapor pressure at constant stress to the change of regain with tension under constant vapor pressure. Derived in a less general manner, it has been used by Treloar [5, 6]. For horse hair and both isotropic and oriented viscose rayon monofilaments, he has shown that there is reasonable agreement between experiment and theory, although an exact quantitative test was not possible. Equation 11 similarly relates the area swelling with vapor pressure to the change of regain under a transverse stress. The direct measurement of transverse pressure on fibers (for example, the fibers in a yarn) would be difficult, if not impossible, but this relation would enable values to be estimated from measurements of the change of regain of the fibers and a knowledge of the swelling behavior. Equations 12 and 13 enable the effects of a combined change of stresses and vapor pressures to be calculated if the swelling behavior and the R.H. regain relation are known.

Equations 14 and 15 enable the changes of dimensions of fabrics with vapor pressure to be related to the change of regain with stress at constant vapor pressure, thus extending the application of a single set of tests. Equations 16 and 17 apply to the general change of conditions.

The application of these equations may be further extended by the general relation between partial differential coefficients:

$$\left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x \tag{18}$$

Thus the stress developed in a piece of fabric held stretched at a constant length under a change of vapor pressure would be given by

$$\left(\frac{\partial X'}{\partial p}\right)_{x'Y'} = -\left(\frac{\partial X'}{\partial x'}\right)_{pY'} \left(\frac{\partial x'}{\partial p}\right)_{x'Y'} \tag{19}$$

From Equation 14,

$$= \frac{vx'}{A'}\left(\frac{\partial X'}{\partial x'}\right)_{pY'} \left(\frac{\partial r}{\partial X'}\right)_{pY'}$$

$$= \frac{vx'}{A'}\left(\frac{\partial r}{\partial x'}\right)_{pY'}$$

The change in stress with vapor pressure could then be obtained either from the modulus of elasticity and the effect of swelling, using Equation 19, or from the relation between regain and dimensions when these are varied by a changing stress at constant vapor pressure.

Summary

A new form of the derivation of the relation between moisture absorption, swelling, and applied stresses has been given and has been used to obtain the equations applicable to textile systems. They are strictly valid only under reversible conditions. Some applications of these equations have been suggested. They may also be of value in dealing with other problems, particularly in relation to the dimensional stability of material under changing

moisture conditions, which is sometimes a serious defect in use [3].

Literature Cited

1. Barkas, W. W., *Trans. Faraday Soc.* **38**, 194 (1942).
2. Gurney, C., *Proc. Phys. Soc.* **59**, 629 (1947).
3. Kaswell, E. R., *Textile Fibers, Yarns, and Fabrics*, Reinhold, New York, p. 292 *et seq.* (1953).
4. Porter, A. W., *Proc. Roy. Soc.* **A79**, 519 (1907).
5. Treloar, L. R. G., *Trans. Faraday Soc.* **48**, 567 (1952).
6. Treloar, L. R. G., *Trans. Faraday Soc.* **49**, 816 (1953).
7. Warburton, F. L., *Proc. Phys. Soc.* **58**, 585 (1946).

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The Relationship of Experimentally Evaluated Lateral Order Distribution to the Skin-Core Effect of Viscose Rayon[1]

Y. Tsuda and S. Mukoyama

Research Center, Toyo Rayon Co., Ltd., Otsu, Shiga, Japan

Abstract

The lateral order distributions of experimental rayons spun in the spinning baths of various compositions are evaluated using the method of fractional dissolution of the methanolized cellulose. They are compared with the skin-core effect of cross section which is characteristic of the structure of viscose rayon.

Introduction

Recently various methods of evaluating experimentally the lateral order (L.O.) distribution of cellulose have been reported [3, 4, 6]. Each of them gave valuable information on the fine structure of cellulose; however, none of them cover completely the real aspect of the L.O. distribution. Therefore, it is significant to elucidate the relationship of the L.O. distribution evaluated by such a method to any fine structure characteristics of cellulose.

In a previous paper [5], the authors have reported the dependency of L.O. distribution of viscose rayon on the composition of the coagulating bath; they also discussed the relationship of the skin-core effect in cross sections and the degree of primary swelling, which are the characteristic properties of the fine structure of viscose rayon.

[1] This article was delivered at the 10th annual meeting of the Chemical Society of Japan, April 1957.

In the present investigation, the same estimating method was adopted with regard to samples of various fine structures; more general conclusions on these relationships were obtained.

Experimental

Cellulose Samples

Four series of experimental viscose rayons were spun in baths of various compositions, as shown in Table I. Degree of primary swelling was obtained by the centrifugal method [1], according to the equation

$$Q = \frac{A - B}{B}$$

where Q is the degree of primary swelling, A is the weight of sample after centrifugation, and B is the weight in the dry state. The skin-core effect of each sample is shown in Figure 1. Azine Brilliant Blue was used as a selective skin staining agent;

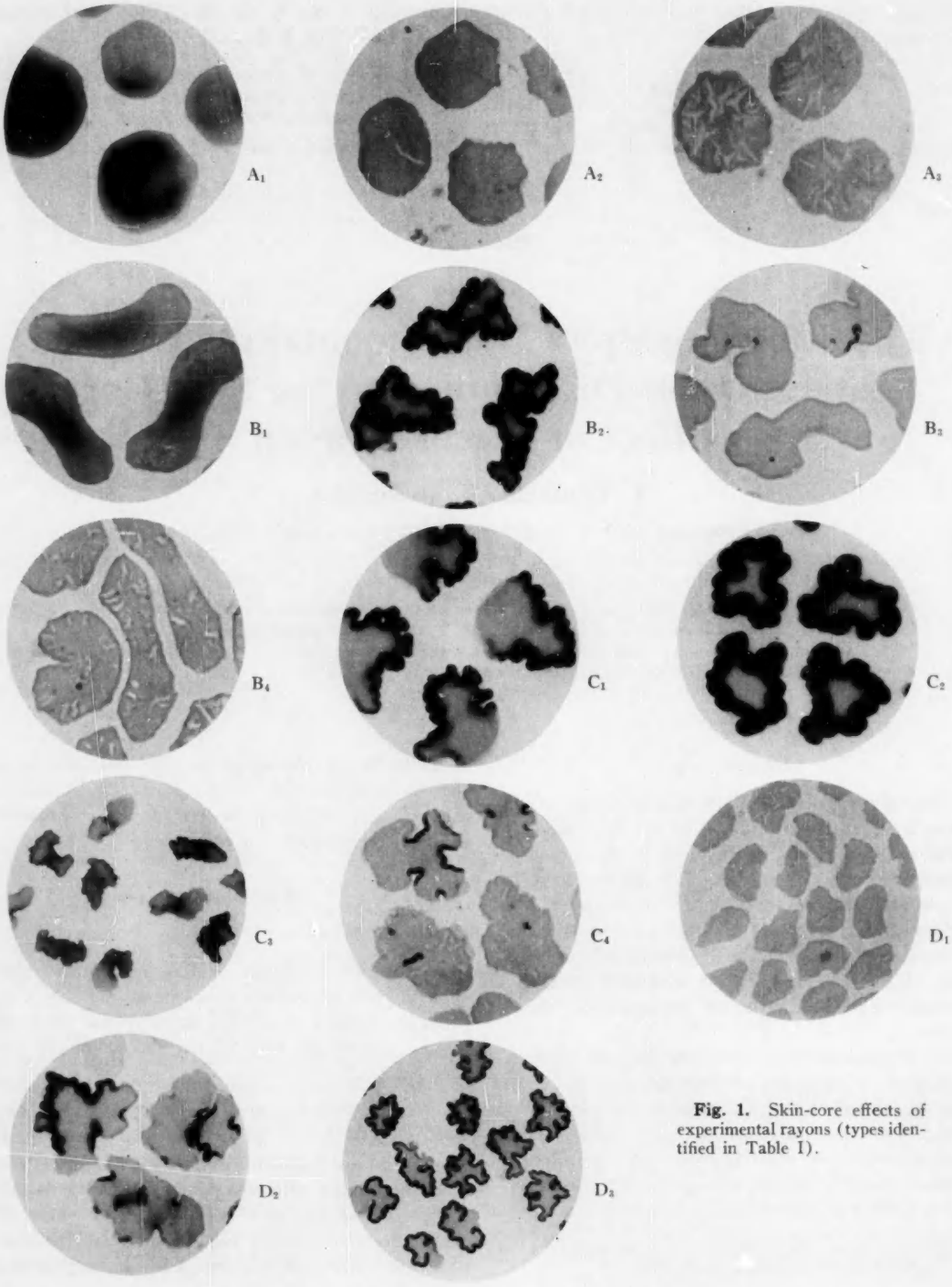

Fig. 1. Skin-core effects of experimental rayons (types identified in Table I).

this staining method is reported in detail by Kato [2] in this journal. In the figure, the skin is the stained part.

Lateral Order Distribution

The same method as reported in a previous paper [3] was employed (see below) with a partial modification; the methanolysis was performed at 40° C. for 24 hr., and the fractional dissolution of the methanolized cellulose in NaOH solutions of various concentrations was performed at 25° C. The L.O. distribution was given by differentiating the solubility curve of the fractional dissolution.

Results and Discussion

The L.O. distributions are shown in Figures 2, 3, 4, and 5. As shown in Figure 2, the higher the concentration of H_2SO_4 of the coagulating bath, the lower the L.O. at the peak of the distribution curve. Although all of these cross sections show the core without the skin, the L.O. distributions are different from each other.

Yarn A_3 (Figure 1) has a cracked core, which is seen also in the cross sections of yarns B_4, C_4, and D_1. All these yarns have a peak of lower order than those yarns which have a normal core. When these yarns are spun it is sure that regeneration predominates over coagulation because of the high concentration of acid in the spinning baths. This suggests that the viscose rayon spun in a spinning mechanism as shown above has a fine structure of low L.O. in general.

In the case of Müller-type bath yarns, various types of the skin-core effect are observed; the L.O. distribution also varies with the variation in skin-core effect. As seen in the L.O. distribution curves of B_2 and C_2, the yarn which has the skin-core struc-

The Fractional Dissolution Method-Methanolysis.—1 *N* hydrogen chloride in absolute methyl alcohol was used as a methanolysis reagent; it was prepared by blowing dry hydrogen chloride gas into dry absolute alcohol. The methanolysis was performed in an Erlenmeyer flask kept at 50° ± 0.1° C. for 48 hr., 6 g. of bone-dry powdered sample being placed in about 250 ml. of reagent. After methanolysis, the sample was filtered, washed with methyl alcohol until it became chloride-free, then dried.

Fractional Dissolution.—Every 0.2 g. of the methanolyzed samples was treated with 20 ml. of sodium hydroxide solutions of increasing concentrations; after being kept at 8° ± 0.1° C. for 2 hr. the undissolved residues were filtered, washed with distilled water until the neutral reaction was obtained, and dried at 105° C. to constant weight.

Lateral Order Distribution.—Solubility Q was defined as follows:

$$Q = 1 - a \cdot m$$

where a represents a fraction of residue at fractional dissolution and m a yield at methanolysis.

Summative mass-order relations were given by plotting Q versus increasing concentrations of sodium hydroxide. The lateral order distribution for the original sample was given by differentiating the mass-order curve.

TABLE I. Spinning Conditions of Experimental Viscose Rayon

Sample	Concentration, %			Degree of primary swelling	Classification of the skin-core effect
	H_2SO_4	Na_2SO_4	$ZnSO_4$		
A_1	4	0	0	3.9	all core
A_2	8	0	0	4.2	all core
A_3	20	0	0	5.2	all core with crack
B_1	5	20	1	3.0	all core
B_2	8	20	1	2.3	skin-core
B_3	12	20	1	3.3	all core
B_4	15	20	1	4.0	all core with crack
C_1	5	20	3	2.8	broken skin
C_2	8	20	3	1.4	skin-core
C_3	12	20	3	3.3	broken skin
C_4	15	20	3	4.1	broken skin with crack
D_1	12	10	0	4.4	all core with crack
D_2	12	20	0	3.0	all core
D_3	12	30	0	1.6	broken skin

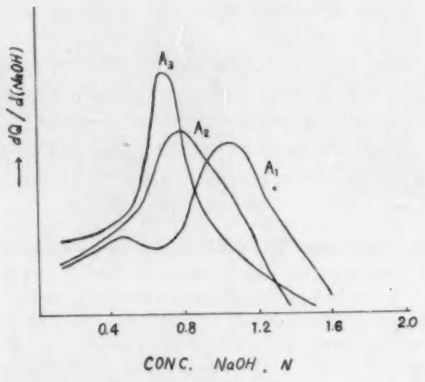

Fig. 2. L.O. distribution curves of A group.

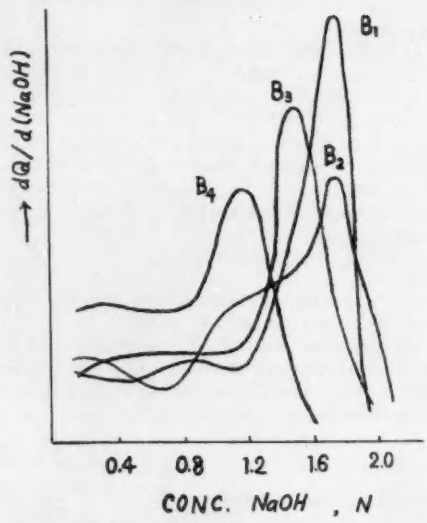

Fig. 3. L.O. distribution curves of B group.

ture has two peaks in the L.O. distribution; it is possible to assign the peak of higher order to the core and the other to the skin. On the other hand, the yarn which has the broken skin structure has a single peak assigned to the core in the L.O. distribution.

As shown in Figure 5, the L.O. of the yarn spun in the bath of H_2SO_4 and Na_2SO_4 depends on the concentration of Na_2SO_4; the higher the concentration of Na_2SO_4, the higher the L.O. of the peak of distribution curve. The skin-core effect varies at the same time, as shown in Figure 1. Yarn D_1 has a cracked core; yarn D_3 has a broken skin structure. Formation of skin in the absence of $ZnSO_4$ in the spinning bath is due to the decrease in activity of the acid in the spinning bath rich in concentration of Na_2SO_4.

It is interesting that comparison of the degree of primary swelling with the L.O. distribution reveals that the higher the L.O. of the peak of the distribution curve, the lower the degree of primary swelling. As shown in Table I, the skin-core structure (B_2 or C_2) corresponds to low values of the degree of primary swelling, which suggests that the skin has lower degree of primary swelling than the core.

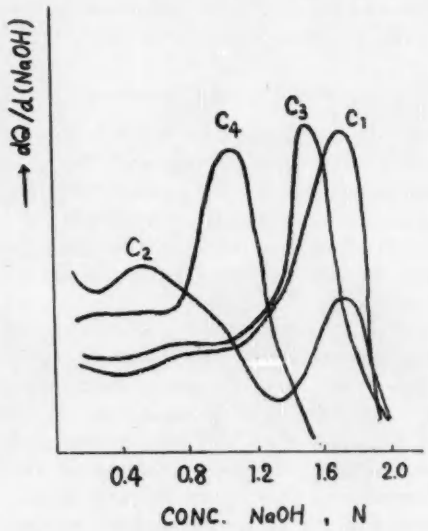

Fig. 4. L.O. distribution curves of C group.

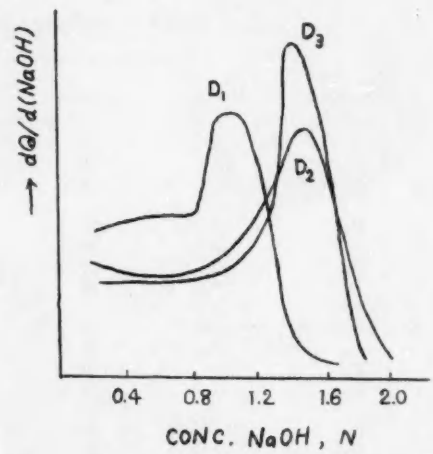

Fig. 5. L.O. distribution curves of D group.

As discussed in a previous paper [5], the L.O. distribution evaluated by this method has an intimate relationship with the skin-core effect in cross sections. This fact suggests that the method is valid to evaluate the crystalline-amorphous multiphase structure of cellulose.

Acknowledgments

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Literature Cited

1. Hubert, E., Matthes, A., and Weisberg, K., *Kolloid Z.* **98**, 173 (1942).
2. Kato, Koichi, TEXTILE RESEARCH JOURNAL **27**, 803 (1957).
3. Maeda, H., *J. Soc. Text. Cellulose Ind. Japan* **12**, 6 (1956).
4. Marchessault, R. H. and Howsmon, J. A., TEXTILE RESEARCH JOURNAL **27**, 30 (1957).
5. Mukoyama, S. and Tsuda, Y., *J. Soc. Text. Cellulose Ind. Japan* **13**, 318 (1957).
6. Tsuda, Y. and Mukoyama, S., *Bull. Chem. Soc. Japan* **29**, 748 (1956).

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The Mode of Operation of Antiredeposition Agents in Detergent Solutions

H. S. Stillo[1] and R. S. Kolat[1]

Technical Service and Development Laboratory, The Dow Chemical Company, Bay City, Michigan

Abstract

Application of colloid stability theory to soil redeposition in detergent liquors has enabled the formulation of a working hypothesis for the effect of polymeric additives on the process. Ionogenic additives are presumed to function by increasing the electrical repulsive forces between soil and fabric, while nonionogenic or weakly ionogenic additives may decrease the attractive dispersion forces or increase the nonelectrical repulsive forces. The electrical repulsive force is inferred from soil redeposition tests to be at a maximum when the zeta potentials of soil and fabric are equal in sign and magnitude. As the difference in zeta potential between the two substrates is increased, an attractive force results, even though the sign of the zeta potential is the same for both substrates. This behavior is attributed to an induced charge effect.

Introduction

The ability of a detergent system to prevent soil redeposition may be as important as its ability to remove soil initially. Certain polymeric materials have been found to be effective in the prevention of soil redeposition when used in extremely small amounts [5, 6]. However, sodium carboxymethyl cellulose (CMC) is the only additive to have achieved widespread acceptance in the detergent industry. Although CMC has proven to be satisfactory in powdered formulations, its incorporation into heavy duty liquid detergent mixtures has presented many problems. Consequently, the recent advent of heavy duty liquid detergent formulations has generated considerable interest in replacements for CMC.

A basic study of soil redeposition was initiated to furnish information that would aid in the development of an antiredeposition agent. Since the process of soil redeposition should be free of many of the complications present in the soil removal process, such a study should afford opportunity for application of theoretical principles.

[1] Present address: Department of Chemistry, Michigan State University, East Lansing, Michigan.

Fong and coworkers [5, 6] have shown that certain nonionogenic polymers such as polyvinylpyrrolidone (PVP) are effective retardants of soil redeposition, but have no effect on the electrophoretic mobilities of a carbon black test soil and cotton in an alkaline detergent solution. In contrast, the ionogenic polymer CMC was found to increase the negative electrophoretic mobility of cotton. These investigators also discovered that PVP was adsorbed on carbon black, and cited evidence [2] that CMC was highly substantive to cotton. Fong and Ward suggested that the nonionogenic additives act at the surface of the carbon black test soil, while CMC or other ionogenic additives act on the surface of cotton and increase the electrostatic repulsion between fabric and soil.

The conclusions of Fong and Ward may be extended by treating the system consisting of removed soil, fabric, and detergent liquor as a colloidal system. This approach enables the interpretation of the effects of additives on soil redeposition in terms of colloid stability theory. The lyophobic colloid stability theory of Verwey and Overbeek [20] and the theory for stability of dispersions in nonpolar media of Mackor and van der Waals [11, 12] have been utilized by the authors of this paper to formulate a working hypothesis of the redeposition process. Durham [4] also has approached the detergency process in a similar manner, although he has utilized the Verwey theory exclusively.

Verwey and Overbeek superimpose the double layer repulsive potential on the attractive potential due to dispersion forces. The zeta potential may justifiably serve as a measure of the repulsive potential, and the action of CMC and other ionogenic additives as reported by Fong and Ward may be attributed to the increase in the repulsive potential rather than merely to a simple electrostatic repulsion.

The above hypothesis, coupled with the experimental work of Fong and Ward, indicates that a comparison of the zeta potentials of cotton and soil in detergent solutions containing polymeric additives should yield useful information on the mode of operation of antiredeposition agents.

Theory

Redeposition of soil in the detergency process consists essentially of the deposition of dispersed particulate soil, which may be considered to be in a colloidal state, onto a fabric in a detergent liquor. Colloidal properties arise from a large value for the ratio of surface area to mass, although this does not, of course, extend to molecular dimensions. Therefore it is reasonable to consider that the fabric, with its very irregular surface and consequently large surface area, should also exhibit colloidal behavior in a detergent bath. On the basis of the above assumption, soil redeposition may be considered as being equivalent to the coagulation of a colloidal dispersion, and colloid stability theory should be applicable.

Origin of the Charge in Colloidal Systems

Colloid stability theory in polar media is based in part on a double layer interaction, the double layer resulting from the acquisition of an electrical charge by a colloidal particle. The particle may acquire such charge in a polar medium either by ionization or adsorption. Many ionogenic substances—for example, proteins and fatty acid soaps—that are capable of existing in the colloidal state become charged as the result of ionization into an ionic group with high charge and small ions of opposite charge.

Materials that are not ionogenic, such as hydrophobic sols, acquire a charge through preferential adsorption of ions present in solution. Adsorption of ions at an interface is attributed to an ion-induced dipole interaction; that is, an ion near a surface induces a dipole in the surface molecules, and an attractive force results. Anions, because of their higher polarizability and lower hydration, have a stronger tendency to be adsorbed than cations. With hydroxyl ions this tendency is particularly strong—due, perhaps, to the formation of hydrogen bonds, which are strong dipole interactions, as well as to the unsymmetrical structure of the ion. Organic salts, such as fatty acid soaps and alkyl-aryl sulfonate salts or other anionic surface active agents, are strongly adsorbed at interfaces in aqueous solution because of the tendency of the nonionogenic or hydrophobic portion of the species to be "squeezed out" of solution by the water dipoles.

The above considerations are particularly applicable to an alkaline detergent solution. Hydrogen bond formation may occur between hydroxyl ions and the hydroxyl groups or ether linkages of the cellulosic fabric in addition to the above adsorption processes. It may also take place between hydroxyl ions and the oxygen complexes on the surface of a carbon soil.

The Zeta Potential

According to the Stern concept, the double layer that results from the acquisition of a charge by a colloidal particle consists of two parts. One is fixed to the surface and is part of the kinetic unit of the particle. It is composed of the adsorbed ions on the surface and a certain number of ions of opposite charge, plus solvent molecules. The second portion contains the remaining compensating ions and is diffuse and mobile. The thickness of the double layer is the distance of charge separation of a nondiffuse double layer having the same electric moment as the actual diffuse double layer.

The potential drop between the surface of the solid and the liquid is the Nernst or thermodynamic potential. It comprises two parts: (1) a sharp drop in potential in the fixed layer, and (2) a gradual drop in the diffuse layer which is termed the zeta potential ζ. By treating the double layer as a condenser of potential ζ, the following relations are obtained:

$$\zeta = \frac{4\pi qd}{D} \tag{1}$$

and

$$\zeta = \frac{4\pi\mu\eta}{D} \tag{2}$$

where q = charge density, d = thickness of the double layer, D = dielectric constant of the medium, η = viscosity, and μ = mobility of the particle.

Equation 1 shows that the zeta potential is a function of both the charge density and the thickness of the double layer. This zeta potential may be calculated from Equation 2 when the mobility is obtained from electrophoretic measurements. Certain errors inherent in the derivation of Equation 2 are reflected in the value thus determined. Subject to this limitation, however, the electrophoretic zeta potential may be identified with the potential drop across the hydrodynamically movable part of the double layer.

Colloid Stability Theory

An important correlation between zeta potential and colloid stability exists. Specifically, there is a value of the zeta potential above which a colloidal sol is relatively stable and below which the sol coagulates rapidly [1, 22]. Although the transition between stability and coagulation is gradual, a general parallelism between zeta potential and stability is obtained. Although the correlation is empirical, the zeta potential is taken to be an approximate measure of the work needed to bring particles close enough to adhere, it being assumed that there is a critical limiting value for a given kind of particle.

In modern colloid theory it is generally assumed that the behavior of colloidal systems is governed by the van der Waals (London) forces and the electrical repulsive forces that arise from the charges on the colloidal particles. Hamaker [1] derived curves of potential energy as a function of distance by superimposing the attractive and repulsive potentials. The particles are stable if the maximum obtained in the resultant curve is much larger than the translational kinetic energy and unstable when the maximum is comparable to or less than this quantity.

A major problem in the approach proposed by Hamaker has been the treatment of the electrical double layer. Various authors have presented conflicting results, even on such simple questions as whether or not the double layer interaction produces attraction or repulsion. Verwey and Overbeek have presented what appears to be the most acceptable treatment. An important result of their theory is that the double layer interaction always results in a repulsive force for a homogeneous system.

The value of the repulsive potential derived by Verwey and Overbeek for identical particles on the basis of the Gouy-Chapman concept of the double layer is essentially a function of the square of the surface potential, i.e., the Nernst potential. Incorporation of the Stern concept of the double layer into the theory leads to the conclusion that the electrophoretic zeta potential will afford a measure of the repulsive potential, since the former, subject to certain errors, has been identified with the potential drop across the diffuse double layer.

The effect of CMC as reported by Fong and Ward was to increase the repulsive forces between fabric and soil. In terms of the above theory, this is the result not of a simple electrostatic effect but rather of a double layer interaction. According to the theory developed thus far, other ionogenic additives that increase the zeta potentials of either the soil or fabric should decrease redeposition. However, Stubblebine [17] has inferred from a correlation of detergency tests and electrophoretic mobilities of soil and fabric in detergent liquors that maximum electrostatic repulsion is obtained when the electro-

phoretic mobilities of fabric and soil are equal. A similar correlation between soil redeposition and zeta potential has been obtained by the authors, and an explanation based on an induced charge effect has been presented in a later section.

Fong and Ward [6] have suggested that nonionogenic additives function by decreasing the attractive forces between fabric and soil as a result of adsorption on soil. This concept has been extended to include adsorption on fabric as well as soil and to provide the mechanism for the reduction of the attractive forces.

The attractive potential between two particles arises from the dispersion forces between individual atoms of the particles. This attractive potential, V_A, is given by

$$V_A = -\frac{\lambda}{d^6} \tag{3}$$

where λ = a constant that is proportional to the polarizability of the two atoms and d = the distance between the atoms.

Although the attractive potential decays rapidly with distance for individual atoms, the potential between two particles decays much more slowly with increasing particle separation as a result of the summation over the attractive potentials of all the atoms in the two particles. For the case of two parallel plates Hamaker [1] gives for the attractive potential

$$V_A = -\frac{A}{48\pi}\frac{1}{d^2} \tag{4}$$

where A is a constant which depends to a certain extent on the materials of the system. Although A would, according to quantum theory, be expected to lie between 10^{-11} and 10^{-14}, in general the value is between 10^{-12} and 10^{-13} [1].

If a nonionogenic additive is to function by decreasing the attractive potential between fabric and soil, either the constant A must be decreased or d must be increased. Although it is difficult to predict the effect on A of additive adsorption on fabric or soil, d should be increased when this occurs. The reduction in attractive force may be attributed to an increase in the minimum permitted distance of approach of fabric and soil as a result of adsorption of the additive on either fabric or soil. A material such as PVP, with bulky groups attached to the polymer chain, might function in this manner.

In addition to the above, it is postulated that the nonionogenic polymers function by increasing a nonelectrical repulsive force. This postulate is based on the Mackor-van der Waals theory of colloid stability in nonpolar media [11, 12]—a theory developed to account for the enhanced stability of colloidal dispersions in hydrocarbons that is obtained by adding aromatic molecules with long aliphatic chains to the system. Van der Waarden [19] has reported that such aromatic-aliphatic compounds stabilize carbon black dispersions in hydrocarbon solvents. The stabilizing effect is enhanced as the chain length of the alkyl group is increased.

Mackor and van der Waals assumed that the presence of electrical repulsion due to the occurrence of an electrical double layer was not important in hydrocarbon media. The stabilizing effect was attributed to a repulsive force that arises from adsorption of the aromatic nucleus of the molecules on the colloidal particles. Such a repulsive force results from the decrease in entropy that is obtained when the particles with adsorbed molecules approach each other. This decrease in entropy causes an increase in the configurational free energy leading to the repulsive force, which at short distances may dominate over the long range dispersion (attractive) forces between the colloidal particles.

The above concept may be applicable to polar media where double layer effects are important, thus necessitating modification of Verwey and Overbeek's theory. If this is done, the decreased attractive force that has been postulated as being due to an increase in the minimum permitted distance of approach may also be considered as an increased nonelectrical repulsive force. In either case the structural requirements of the polymer are similar; that is, a main chain with many long or bulky attached side chains or groups. From either viewpoint the net result is enhanced stability or decreased soil redeposition.

The effect of soil particle size has not been considered in this paper. However, it must be noted that particle size may play an important role in soil redeposition. Probably the most significant theoretical treatment of the effect of particle size has been given by Durham [4], who employed the Verwey-Overbeek theory exclusively. In general, for a given value of the surface potential, stability diminishes as the particle size decreases. Durham has suggested that, since many of the studies of detergency have been made with carbon blacks with

average particle sizes of 30–50 mμ, the lack of stability of the small particles may obscure other phenomena. The experimental work reported in this paper was performed with Aquadag, a graphite dispersion with a particle size of the order of one micron [21]. Since the stability of an Aquadag dispersion should then be much greater than those of smaller-particle carbon blacks for a given value of the surface potential, the behavior suggested by Durham probably was minimized.

Experimental

Soil Deposition Test

Soil redeposition was evaluated by photometric measurement of carbon deposition on cotton cloth (bleached, unsized Indianhead muslin, Testfabrics, Inc.). A Hunter photovolt Model 610 Reflectometer, standardized with an enameled standard as 76% of the reflectance of a magnesia block, was employed. A Terg-O-Tometer (U. S. Testing Company, Inc.) was used to effect carbon deposition on the cotton swatches.

Four unsoiled cotton swatches measuring 5 × 5 in. were agitated in a liter of standard detergent solution that contained 0.05% Aquadag (a graphite paste, 22% solids, Acheson Colloids Company) for 10 min. at 100 cycles/min. and at a temperature of 120° F. The swatches were then given a brief hand rinse in deionized water and agitated for 5 min. in 1 l. of deionized water in the Terg-O-Tometer at 100 cycles/min. and approximately 100° F. The swatches were pressed dry and the reflectance of both sides of each swatch was determined. The average of the eight readings was utilized.

Percent whiteness retention (W.R.) was calculated from

$$\text{Percent W.R.} = \frac{\text{Reflectance of Soiled Cloth}}{\text{Reflectance of Unsoiled Cloth}} \times 100$$

The percent increase in W.R. effected by the polymeric additives was defined as

$$\frac{(\%\ \text{W.R. with Additive}) - (\%\ \text{W.R. without Additive})}{(\%\ \text{W.R. without Additive})} \times 100$$

The standard detergent solution was identical to that employed by Fong and Lundgren [5]. It consisted of 0.12% Nacconol NRSF (an alkyl benzene sulfonate, National Aniline Division, Allied Chemical & Dye Corp.), 0.08% sodium tripolyphosphate (Victor Chemical Works), and 0.04% sodium carbonate (reagent grade) in deionized water. The weight ratio of fabric to wash liquor was 1:100. The concentration of carbon in the wash liquor was 0.011%.

Electrophoretic Determinations

A Tiselius Electrophoresis Apparatus Model 38 (Perkin Elmer Corporation) was employed for the electrophoretic determinations. The mobilities of carbon and several polymeric materials were determined in a standard alkaline buffer solution which consisted of 0.08% sodium tripolyphosphate and 0.04% sodium carbonate. The zeta potentials of carbon and cotton in the presence of a number of whiteness retention additives were calculated from electrophoretic mobilities that were determined in an alkaline detergent solution identical to that described in the preceding paragraph.

The temperature of the determinations was maintained at 32–34° F. by means of an ice bath. The current was adjusted so that the potential gradients were approximately 1.9, 2.7, and 4.9 v. $cm.^{-1}$ for mobility determinations in the alkaline buffer solution, for mobility determinations of carbon in the standard detergent solution, and for mobility determinations of cotton in the standard detergent solution.

The carbon concentration in all determinations was 0.011% (0.05% Aquadag). The cotton was supplied by W. Fong in the form of a powder which had been prepared by Wiley-milling the fabric and grinding it in a vibratory ball mill similar to that described by Forziati et al. [7]. The ground cotton was added to the detergent solution,[2] stirred, and allowed to settle for 10 min. The portion remaining

[2] These materials were used: (1) alpha Protein, a protein derived from defatted soy bean flakes, proximate analysis 88.7% protein, 8.5% moisture, The Glidden Co., Soya Products Division. (2) Carbowax 20M, a polyethylene glycol, Carbide and Carbon Chemicals Co. (3) Kelgin F, sodium alginate, Kelco Co. (4) Marasperse N, sodium lignosulfonate, Marathon Corp. (5) Polyvinylpyrrolidone K-20 (PVP), General Analine and Film Co. (6) Prosein, similar to alpha Protein, proximate analysis 53.5% protein, 4.8% moisture, 2.3% fiber, and 0.9% fat, The Glidden Co., Soya Products Division. (7) Sodium carboxymethyl cellulose (CMC), CT grade, medium viscosity, 75% active; 120, medium viscosity, degree of substitution equal to 1.20–1.40,

suspended was employed for the determinations. The ratio of suspended cotton to detergent liquor was 0.7:100. Since the dispersions of cotton and carbon were opaque, the limit of the opaque zone was used for determination of mobility.

Kinematic viscosity was determined by means of Ostwald viscometers and converted to absolute viscosity directly, since the density of the solutions had a value of 1.00 g.cm.$^{-3}$, and the accuracy of the electrophoretic measurements did not warrant further correction for density. A dielectric constant of water (32° F.) of 88.2 was employed to calculate the zeta potential. It represented an average calculated from two sets of data [3, 23].

The concentrations of CMC CT medium viscosity and sodium cellulose sulfate were corrected for the percent of active ingredient. All other concentrations are reported on an "as is" basis. Concentrations are reported as percentages on the basis of weight of solute per volume of solution, i.e., 1 g. of solute dissolved in sufficient solvent to give 100 ml. of solution is termed a 1% solution.

Results and Discussion

Electrophoretic Mobilities of Additives

Mobilities of several polymers in an alkaline buffer solution consisting of 0.08% sodium tripolyphosphate and 0.04% sodium carbonate were determined to characterize their inherent electrophoretic properties, without the complications caused by interaction with the surface active agent, as reported by Fong and Ward [6]. It was necessary to employ much higher additive concentrations than were used in soil deposition tests in order to obtain stable boundaries. As part of the preliminary electrophoretic work, the mobility of carbon black in alkaline solution containing the whiteness retention additives in the same high concentrations was determined. The concentration of carbon was 0.011%.

The mobilities were calculated from descending boundary data, which are less subject to error than those of the ascending boundary [10]. In order to correct for viscosity effects the mobilities were multiplied by the ratio η' defined as

$$\frac{\text{Viscosity of Buffer Solution that Contains Polymer}}{\text{Viscosity of Buffer Solution}}$$

This correction is similar to that employed by Longsworth and MacInnes [10] in comparing the mobilities of the same protein which were determined at different concentrations (therefore, different viscosities). This correction may be justified, since the experimental mobility—which is nothing more than the velocity of the particle under a potential gradient of one volt per centimeter—is being employed as a basis for the inference of the electrical charge carried by the particle. If the motion of the polymer species is impeded by solvation, which results in an increased viscosity, the inferred charge could not be compared with that of a polymer which does not affect the viscosity to the same extent as a result of solvation. The viscosity correction, although it may not be exactly correct, may be sufficiently accurate for the qualitative inferences which are drawn. The viscosity correction was also applied to the mobilities of carbon, which were determined in the presence of several polymers. Solvation of the carbon particle probably is not important, but allowance must be made for the difference in frictional forces that oppose movement of the particle in media of different viscosities. In this case the medium is the liquid phase, consisting of solvent, buffer, and polymer. The medium is considered as being continuous with respect to the carbon particles, which are much larger than molecular dimensions.

Results are summarized in Table I; all mobilities are negative; that is, the boundaries moved toward the positive electrode. The nonionogenic polymers had no electrophoretic mobility. Sodium carboxymethyl cellulose exhibited a high mobility, while the other ionogenic polymers, with the exception of Kelgin F, possessed a considerably lower mobility. The descending boundary of Kelgin F was not stable, but an estimate of the mobility was afforded by comparison of the mobilities calculated from the ascending boundaries for CMC and Kelgin F. Thus determined, the value of the product $\eta'\mu$ for Kelgin F was 210×10^{-5} cm.^{2} v.$^{-1}$ sec.$^{-1}$, while that for CMC was 190×10^{-5} cm.^{2} v.$^{-1}$ sec.$^{-1}$. Although Marasperse N contains the highly polar sulfonate group, its mobility was much lower than that of CMC.

Hercules Powder Co. (8) Sodium cellulose sulfate, degree of substitution equal to 0.36; viscosity of a 2.0% aqueous solution at 25° C. eqnal to 19.0 cps.; 95.2% active and 4.8% water, Tennessee Eastman Corp., and (9) The following experimental polymers from The Dow Chemical Co.: Polyethylene Glycol (PEG), molecular weight approximately 30,000; Copolymer: 7.5% propylene oxide and 92.5% ethylene oxide (PO–EO); Copolymer: 50% acrylic acid and 50% acrylamide (PAA–AAM); and Polymonovinylether of diethylene glycol (PMVDEG).

This appears reasonable when one considers that the bulky structure of Marasperse N probably results in a quite low charge density.

Correlation of whiteness retention results with electrophoretic data will be deferred to a later section, in which data determined with additives at concentrations equivalent to those employed in soil deposition tests will be presented. However, certain conclusions may be drawn from the mobilities of carbon black presented in Table I. Since the product $\eta'\mu$ is greater for CMC than for carbon with no additive and is also greater for carbon in a solution containing CMC than in one that does not, one can infer that CMC at the high concentrations employed is adsorbed on carbon. Adsorption of CMC by carbon and other soils has been shown to occur by Stüpel [18]. However, it will be shown in a later section that the inference of adsorption of CMC by carbon cannot be made when CMC is employed at much lower concentration.

The nonionogenic and some ionogenic materials, i.e., Marasperse N and alpha Protein, retard the mobility of carbon even when the effect of viscosity is considered. The retardation is attributed to a displacement of adsorbed hydroxyl or polyphosphate anions from the carbon surface by the neutral or slower ionogenic polymers. Indeed, the charge on carbon was completely displaced by Carbowax 20M. These retardation effects were also noticed at lower concentrations of additive, as will be discussed in a later section.

Effect of Polymeric Additives on Soil Redeposition

The additives were employed at several concentrations in the standard detergent solution consisting of 0.12% Nacconol NRSF, 0.08% sodium tripolyphosphate, and 0.04% sodium carbonate. With most of them, comparatively high concentrations were required in order to equal the activity of a 0.002% CMC CT Med. solution. This CMC concentration is the same as would be obtained by using 2 g./l. of a detergent formulation containing 1% CMC. The results obtained are summarized in Table II.

An appreciable amount of variation exists in the whiteness retention values for zero additive. This may be attributed partly to fluctuations in the nature of the unsoiled cloth and perhaps to variation of the quality of the carbon black dispersion. The results reported for various concentrations of a particular additive were all obtained employing the same stock solutions of materials and the same stock dispersion of carbon black and unsoiled cloth cut from the same section of a roll.

In general, antiredeposition activity increased with increasing additive concentration. A notable exception to this behavior was Carbowax 20M, which had maximum whiteness retention activity at 0.002% but promoted soil deposition at somewhat higher concentrations. This action may be attributed to a displacement of the surface charge of carbon (Tables I and III). It will be shown in a later section that Carbowax 20M functions by decreasing the attractive forces without affecting the electrical character-

TABLE I. Electrophoretic Mobilities of Carbon and Polymeric Additives in an Alkaline Buffer Solution Without Surface Active Agent *

Polymeric additive, %	Viscosity, η, at 32° F., centistokes	η'	Mobility†, $\mu\times10^5$, cm.² v.$^{-1}$ sec.$^{-1}$		$\eta'\mu\times10^5$, cm.² v.$^{-1}$ sec.$^{-1}$	
			Polymer	Carbon	Polymer	Carbon
None	1.836	1.000	—	19	—	19
0.50 CMC CT Med.	9.728	5.298	22	11	120	58
0.50 Marasperse N	1.849	1.007	19	12	19	12
0.25 Kelgin F	14.007	7.629	‡	10	‡	76
0.25 alpha Protein	2.064	1.124	6.6	6.7	7.4	7.5
0.50 PVP K–20	1.968	1.072	nil	5.6	nil	6.0
0.10 PO–EO	1.939	1.056	nil	2.5	nil	2.6
0.50 Carbowax 20M	2.448	1.333	nil	nil	nil	nil
0.10 Carbowax 20M	1.933	1.053	—	nil	—	nil

* Composition of buffer solution: 0.08% sodium tripolyphosphate and 0.04% sodium carbonate.
† Mobilities are negative and are calculated from the descending boundary.
‡ Descending boundary was not stable.

istics of cotton and carbon when employed at a concentration of 0.002%. At higher concentrations, the advantage gained by a decrease in the attractive forces is removed by the decrease in repulsive force that accompanies the loss of surface charge of carbon. However, it should be noted that the inference of displacement of surface charge by Carbowax 20M when employed at higher concentrations is based on electrophoretic data obtained in the buffer solution which did not contain surface active agent, while the soil deposition tests did employ surface active agent. The validity of the inference is limited by the extent to which the surface active agent may modify the behavior of Carbowax 20M.

The materials PAA–AAM and Kelgin F increase redeposition at all concentrations employed and will be discussed in a later section. No appreciable increase is observed with increasing concentration of PMVDEG; this behavior may be attributed to the low molecular weight of the polymer (less than 1000). Such short chain polymers may undergo intermolecular association, with the result that coverage of the surface of the fabric or soil is not increased by further addition of polymer.

The evaluation of the effectiveness of antiredeposition agents is quite difficult. A major objection to tests which employ an unrealistically high concentration of soil is that the effects of antiredeposition agents whose major action is on the soil may be exaggerated in both a positive and negative sense. Saunders and Sanders [15] recently have reported that dispersions, when stabilized by the adsorption of a nonionogenic material which decreases the zeta

TABLE II. Effect of Polymeric Additives on Whiteness Retention *

Percent Whiteness Retention

Additive	Concentration of additive, %			
	0.000	0.002	0.010	0.050
Prosein	60.8	69.6	77.3	76.8
alpha Protein	61.6	66.7	71.2	77.0
CMC CT Med.	60.8	75.5		
PVP K–20	60.8	70.9	75.0	82.5
PO–EO	55.2	60.4	62.3	66.1
Sodium cellulose sulfate	68.5	82.4	84.4	85.7
CMC 120 Med.	69.4	80.7	85.1	85.7
Marasperse N	61.4	63.1	67.5	71.0
PEG	60.2	67.4	66.6	69.6
Carbowax 20M	60.4	63.9	62.9	57.4
Kelgin F	57.3	56.4	54.2	41.4
PAA–AAM	51.6	49.2	42.7	32.9
	Concentration of additive, %			
	0.000	0.0005	0.001	0.002
PMVDEG	58.6	70.7	71.3	67.0

* Composition of the standard detergent solution: 0.12% Nacconol NRSF, 0.08% sodium tripolyphosphate, and 0.04% sodium carbonate.

TABLE III. Zeta Potentials of Carbon and Cotton in the Presence of Surface Active Agent and Polymeric Additives *

Additive	Conc. of additive, %	Viscosity** at 32° F., centistokes	Zeta potential, negative volts		% Increase in whiteness retention
			Carbon	Cotton	
None	—	1.830	0.042	0.028	—
Prosein	0.01	1.830	0.041	0.021	27.0
CMC CT Med.	0.002	1.829	0.042	0.044	24.2
PVP K–20	0.01	1.836	0.041	0.025	23.1
PO–EO	0.05	1.843	0.031	0.015	19.8
Sodium Cellulose Sulfate	0.002	1.852	0.040	0.032	18.7
CMC 120 Med.	0.002	1.866	0.041	0.050	16.3
Marasperse N	0.05	1.825	0.037	0.017	15.6
PEG	0.05	1.868	0.024	0.014	15.6
PMVDEG	0.002	1.842	0.041	0.020	14.3
Carbowax 20M	0.002	1.834	0.040	0.020	5.8
Kelgin F	0.05	3.120	0.056	0.033	−27.5
PAA–AAM	0.05	4.152	0.096	0.042	−56.8

* Composition of the standard detergent solution: 0.12% Nacconol NRSF, 0.08% sodium tripolyphosphate, and 0.04% sodium carbonate.

** The tabulated values of the viscosity of the standard detergent solution with the indicated additive were employed to calculate the zeta potentials by means of Equation 2.

potential (electrical repulsive potential) but exerts a protective colloid action, may be rendered unstable if an amount of additive insufficient to completely cover the particles is added. The efficacy of an antiredeposition agent with comparatively poor soil adsorption characteristics may thus appear poorer in a soil redeposition test of the type employed in this work than is actually the case. On the other hand, a material with exceptionally good soil adsorption characteristics would tend, as long as the amount of additive was adequate to completely cover the soil, to be favored by a high soil concentration over materials that acted on the fabric. The protective colloid action cited above may correspond to a decrease in the attractive forces or to an increase in the nonelectrical repulsive forces.

Zeta Potential of Carbon and Cotton in the Presence of Whiteness Retention Additives

The zeta potentials of carbon and cotton in the standard detergent solution containing whiteness retention additives were determined for concentrations of additives at which appreciable activity was exhibited (Table III).

The possession of negative values for the zeta potential of the two substrates in an alkaline detergent solution is in accord with literature data [6], and is expected in view of the preferential adsorption of anions. In addition to the data of Table III, the zeta potential of carbon in a solution consisting of 0.04% sodium carbonate and 0.08% sodium tripolyphosphate was calculated as −0.045 volts from the data of Table I. This value agrees quite well with that obtained when the surface active agent is added, i.e., −0.042 volts, and indicates the importance of the builder anions in contributing to the electrical nature of the substrates.

No general correlation exists between zeta potential of fabric and soil and efficacy of antiredeposition agent. This conclusion was expected on the basis of the proposed modes of action of antiredeposition agents, since both ionogenic and nonionogenic materials were included. However, the agents may be classified on the basis of a significant effect on the zeta potentials of carbon and cotton (Table IV). The difference between the zeta potential with and without additive was considered significant if twice the value of the standard deviation was exceeded. The standard deviation was ±0.003 volts for the carbon determinations and ±0.004 volts for the cotton determinations.

TABLE IV. Classification of Whiteness Retention Additives *

Group A—No effect on zeta potential of either cotton or carbon.

Additive
Prosein
PVP K–20
Sodium cellulose sulfate
PMVDEG
Carbowax 20M

Group B—Significant effect on zeta potential of either cotton or carbon or both.

Additive	Carbon	Cotton
CMC CT Med.	None	Increase
PO–EO	Decrease	Decrease
CMC 120 Med.	None	Increase
Marasperse N	None	Decrease
PEG	Decrease	Decrease
Kelgin F	Increase	None
PAA–AAM	Increase	Increase

* A classification on the basis of the effect of the additives on the zeta potentials of cotton and carbon in the standard detergent solution consisting of 0.12% Nacconol NRSF, 0.08% sodium tripolyphosphate, and 0.04% sodium carbonate.

Several of the nonionogenic additives, i.e., PO–EO and PEG, decreased the zeta potentials of both cotton and carbon, while Carbowax 20M (in the standard detergent solution which contained surface active agent) did not affect the zeta potentials of either. The decrease may be attributed to the displacement of adsorbed ions from the surface of cotton and carbon. The difference between PEG and Carbowax 20M may result from the differences in magnitude and distribution of molecular weights, which might alter the adsorption characteristics.

Although an ionogenic material, sodium cellulose sulfate, in contrast to the CMC polymers, does not affect the zeta potentials. However, the degree of substitution (D.S.) of cellulose sulfate is 0.36 as compared to a value of approximately 0.5–0.6 for CMC CT Med. and 1.20–1.40 for CMC 120 Med. The effect of degree of substitution is also apparent from a comparison of the zeta potential of cotton with each of the two CMC polymers—it is increased more by CMC 120 Med. than by CMC CT Med.

Since the zeta potential of cotton is increased by both CMC CT Med. and CMC 120 Med., it can be inferred that CMC is adsorbed by cotton. It is not possible to infer that CMC at a concentration of

0.002% is adsorbed by carbon, in contrast to the data of Table I, which was obtained for CMC CT Med. in an alkaline buffer solution without surface active agent and at a much higher concentration of CMC. The authors are aware, however, that contradictory reports of adsorption of CMC by the substrates cotton and carbon have been presented. Bartholomé and Buschmann [2] have reported that CMC is highly substantive to cotton, while Stüpel [18] has found by means of fluorescence microscopy that CMC was adsorbed on carbon and other soils but not on cotton. Stawitz, Klaus, and Kramer [16], who employed radioactive techniques, likewise found that CMC was not adsorbed on cotton to any extent.

Although the above classification does not render evident a correlation between zeta potential and whiteness retention, a basis is provided for attributing the effectiveness of the materials in Group A to a reduction of the attractive dispersion forces (or increasing the nonelectrical repulsive forces) between soil and fabric. The polymers in Group B are discussed below.

Relation of Zeta Potential Difference to Whiteness Retention

On the basis of colloid stability theory, in which the zeta potential was assumed to be the quantity that determines the repulsive potential, a correlation was expected between the magnitude of the zeta potentials of carbon and cotton and whiteness retention. The predicted behavior was that an increase in the zeta potential of carbon or cotton would result in the inhibition of soil redeposition. However, the data of Tables III and IV show that such is not the case. Marasperse N, PO–EO, and PEG, which are effective in retarding soil redeposition, decrease the zeta potentials of either cotton or carbon or both. More striking is the observation that Kelgin F and PAA–AAM, which accelerate soil redeposition, increase the zeta potentials of cotton and carbon. In addition, CMC 120 Med. increases the zeta potential of cotton more than does CMC CT Med., and yet the latter is more effective.

The behavior of the CMC polymers does not agree with the explanation proposed by Nieuwenhuis [14] for the effect of D.S. on the efficacy of CMC. Nieuwenhuis has proposed that a D.S. which is too high will result in decreased adsorption of CMC chains on the cellulose fabric, and that the charge density of the fabric will be less than with a polymer of lower D.S. Apparently the steric effects that were presumed to hinder adsorption of the highly substituted CMC may not be as important as Nieuwenhuis believed.

The existence of a correlation between zeta potential and whiteness retention is suggested by the work of Stubblebine [17] on the relation of detergency to the electrophoretic mobilities of cotton and carbon. The concept utilized by Stubblebine was that maximum electrostatic repulsion is obtained

TABLE V. Relation of the Difference Between the Zeta Potential of Carbon and Cotton to Whiteness Retention *

% Whiteness retention additive	Viscosity** at 32° F., centistokes	Zeta potential, negative volts		Diff. in zeta pot., volts	% Increase in whiteness retention
		Carbon	Cotton		
0.002 CMC CT Med.	1.829	0.042	0.044	0.002	24.2
0.05 PO–EO	1.843	0.031	0.015	0.016	19.8
0.0067 CMC 120 Med. 0.05 Kelgin F	3.294	0.079	0.083	0.004	16.5
0.002 CMC 120 Med.	1.866	0.041	0.050	0.009	16.3
0.05 PEG	1.868	0.024	0.014	0.010	15.6
0.05 Marasperse N	1.825	0.037	0.017	0.020	15.6
0.0027 CMC 120 Med. 0.05 Kelgin F	3.163	0.061	0.077	0.016	6.2
None	1.830	0.042	0.028	0.014	—
0.05 Kelgin F	3.120	0.056	0.033	0.023	−27.5
0.05 PAA–AAM	4.152	0.096	0.042	0.054	−56.8

* The standard detergent solution consisting of 0.12% Nacconol NRSF, 0.08% sodium tripolyphosphate, and 0.04% sodium carbonate was employed.

** The tabulated values of the viscosity of the standard detergent solution with the indicated additive were employed to calculate the zeta potentials by means of Equation 2.

when the electrophoretic mobilities of cotton and carbon are equal. Table V summarizes the results, correlating the differences in zeta potential between carbon and cotton and whiteness retention.

Materials that had no effect on either the zeta potential of carbon or cotton were not included in this tabulation, since it was assumed that these additives functioned primarily by decreasing the attractive potential or increasing the nonelectrical repulsive potential. This behavior would not be reflected in zeta potential measurements. Electrophoretic measurements and whiteness retention activity determinations of mixtures of CMC 120 Med. and Kelgin were made in the belief that, since CMC 120 Med. increased the zeta potential of cotton above that of carbon and Kelgin increased the zeta potential of carbon, mixtures of the two additives would be effective antiredeposition agents. These results are included in the tabulation and increase the completeness of the range of the data.

Except for Marasperse N and PO–EO, the data of Table V show that whiteness retention varies inversely as the difference in zeta potential between carbon and cotton. It is reasonable to attribute the failure of Marasperse N and PO–EO to follow this correlation to differences in effects on attractive dispersion forces. It is presumed that such differences in the effects on attractive dispersion forces are absent for the polymers that do follow the correlation. A basis for this assumption is afforded by the chemical similarity of these materials; with the exception of PEG they are all polycarboxylic substances.

The data strikingly point out the uniqueness of CMC CT Med., which is the only material that equalized the zeta potentials of cotton and carbon. With other types of fabric, CMC is not as effective [6, 8, 14], perhaps because the zeta potential is not equalized. This relation may be considered further with respect to the use of dyed ground cotton as a soil. If for example, it is assumed that the surface characteristics of the dyed ground cotton are similar to those of undyed whole fabric so that the zeta potentials of the two materials are equal, redeposition acceleration should not occur with additives such as Kelgin and PAA–AAM when dyed cotton is used as a soil. In fact, with the latter whiteness retention should be increased, since the zeta potential of cotton is increased by PAA–AAM. On the other hand, Kelgin, which does not affect the zeta potential, should not alter whiteness retention. The predictions are borne out by the data of Table VI.

TABLE VI. Deposition of Dyed Cotton Powder on Undyed Fabric *

Additive	Conc. of additive, %	% Increase in whiteness retention
CMC CT Med.	0.002	7.9
Kelgin F	0.05	0.5
PAA–AAM	0.05	2.8

* Composition of standard detergent solution: 0.12% Nacconol NRSF, 0.08% sodium tripolyphosphate, and 0.04% sodium carbonate.

The usual deposition test procedure was altered somewhat for the above tests. Although the standard detergent solution in deionized water was employed, the washing was carried out at 175 cycles/min. for 20 min., while the rinsing was at 100 cycles/min. for 5 min. Dyed cotton powder that passed through a 200 mesh sieve was used as the soil at a concentration of 3 g./l. Calcosol navy blue paste, a vat type dye, was employed to dye the cotton powder.

Induced Charge Effect

Although the correlation obtained by Stubblebine between detergency and difference in electrophoretic mobility of soil and fabric was confirmed by the correlation between whiteness retention and zeta potential difference, an explanation for this behavior is required.

The correlation may be explained on the basis of an induced charge mechanism. Qualitatively, an attractive force between two particles that carry a mobile charge of the same sign but different in magnitude may result if one particle induces a charge of opposite sign in the other particle. The magnitude of the induced charge, and consequently the magnitude of the attractive force, would depend on the original difference in charge between the two particles and on the difference in polarizability of the charge on the two particles.

Although the redeposition process involves the more complicated double layer interaction, an analogous charge induction process may occur as a result of polarization of the charge, i.e., displacement of the ions of the double layer. In the double layer case the dipole moment per unit area, i.e., the product of charge density and thickness of the double layer, is

involved rather than the charge density. Since the zeta potential is a measure of the dipole moment per unit area (Equation 1), the attractive force is a function of the zeta potential difference and the difference in polarizability of the double layers associated with the two substrates. Charge redistribution in the solid phase may also be important. The data presented in this paper allow only the deduction of the relation between zeta potential difference and the attractive force as inferred from whiteness retention activity. In the cases studied, differences in polarizability and charge redistribution in the solid phases did not mask the relation between zeta potential difference and whiteness retention activity.

The induced charge mechanism postulated above is analogous to the inductive conversion of a nonpolar molecule to a dipole by means of an ion or polar molecule, with a resultant attractive force. In dipole induction the electron density of the molecule is altered, while in the colloidal case the displacement of ions in the double layer occurs. A procedure similar to J. G. Kirkwood's treatment of protein interactions [9], in which an attractive force between two molecules is obtained as the result of interaction between the fluctuating charges and multiple moments of the two protein molecules, may possibly be applicable to a quantitative description of the induced charge effect.

Conclusion

The system consisting of dispersed soil and fabric in detergent liquor may be treated as a colloidal system. This enables the application of colloid stability theory, and a working hypothesis of the soil redeposition process may be formulated on the basis of theory. Colloid stability or soil redeposition is governed by the resultant of three component forces: (1) an electrical force which may be either attractive or repulsive and that is due to a double layer interaction, (2) an attractive force that arises from the London or dispersion forces, and (3) a nonelectrical repulsive force that is due to a nonelectrical interaction of the surface adsorption layers of the particles.

It is postulated that ionogenic whiteness retention additives such as CMC function primarily by increasing the electrical repulsive force as a result of being adsorbed on soil and/or fabric. Nonionogenic additives such as PVP and weakly ionogenic additives such as proteins or polyelectrolytes of low degree of substitution are also presumed to function through adsorption on the substrates, but in most cases the major effect of these materials is to lower the nonelectrical attractive forces or increase the nonelectrical repulsive forces. The decrease in the nonelectrical attractive forces is attributed to an increase in the minimum permitted distance of approach of soil and fabric, while the other is attributed to a decrease in the configurational entropy that would result from deposition of soil; in either case the function of the additive is steric in nature.

In an alkaline detergent solution the zeta potentials of both cotton and carbon have a negative value, but they are not equal in magnitude. Although this potential may be taken as a measure of the repulsive potential, soil redeposition is not a function simply of the magnitude of the zeta potentials of the soil and fabric, but depends also on their difference. This behavior may be attributed to an induced charge effect which arises from the difference in zeta potential even though the signs may be the same. It is postulated that an electrical attractive force results from this interaction. Although a difference in the polarizability of the double layers of the two substrates may also contribute to the induced charge effect, the extent to which this may occur was not apparent from the available data. Sodium carboxymethyl cellulose (CT medium viscosity) was unique in that it equalized the zeta potentials of carbon and cotton in an alkaline detergent solution. The results suggest that any ionogenic polymer capable of adsorption on fabric or soil may have antiredeposition activity if the degree of substitution is modified so that the zeta potentials of the two substrates are equalized.

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Literature Cited

1. Alexander, A. E. and Johnson, P., *Colloid Science*, Vol. I, Oxford University Press, London, pp. 114–27 (1949).
2. Bartholomé, E. and Buschmann, K. F., *Melliand Textilber.* **30**, 249 (1949).

3. Drake, F. H., Pierce, G. W., and Dow, M. T., *Phys. Rev.* **35**, 613 (1930).
4. Durham, K., *J. Appl. Chem.* **6**, 153–61 (1956).
5. Fong, W. and Lundgren, H. P., TEXTILE RESEARCH JOURNAL **23**, 769–75 (1953).
6. Fong, W. and Ward, W. H., *Ibid.* **24**, 881–9 (1954).
7. Forziati, F. H., Stone, W. K., Rowen, J. W., and Appel, W. D., *J. Research Nat. Bur. Standards* **45**, 109–13 (1950).
8. Hart, W. J. and Compton, J., TEXTILE RESEARCH JOURNAL **23**, 164–8 (1953).
9. Kirkwood, J. G. and Shumaker, J. B., *Proc. Nat. Acad. Sci. U. S.* **38**, 863–71 (1952); 855–62 (1952).
10. Longsworth, L. G. and MacInnes, D. A., *J. Am. Chem. Soc.* **62**, 705–11 (1940).
11. Mackor, E. L., *J. Colloid Sci.* **6**, 492–5 (1951).
12. Mackor, E. L. and van der Waals, J. H., *Ibid.* **7**, 535–50 (1952).
13. MacInnes, D. A., *The Principles of Electrochemistry*, Reinhold Publishing Corp., New York, p. 144 (1939).
14. Nieuwenhuis, K. J., *J. Polymer Sci.* **12**, 237–52 (1954).
15. Saunders, F. L. and Sanders, J. W., *J. Colloid Sci.* **11**, 260–71 (1956).
16. Stawitz, J., Klaus, W., and Kramer, H., *Kolloid Z.* **142**, 166 (1955).
17. Stubblebine, W., "A Study of the Electrophoretic Mobility of Carbon, Cotton, and Wool in Aqueous and Nonaqueous Detergent Solutions," Ph.D. Thesis, Penn. State U. (1942).
18. Stüpel, H., *Melliand Textilber.* **36**, 335 (1955).
19. van der Waarden, M., *J. Colloid Sci.* **5**, 317 (1950); **6**, 443 (1951).
20. Verwey, E. J. and Overbeek, T. T. G., "Theory of the Stability of Lyophobic Colloids," Elsevier Publishing Co., New York (1948).
21. Vitale, P. J., *J. Am. Oil Chemists' Soc.* **31**, 341 (1954).
22. Weiser, H. G., *Colloid Chemistry*, 2nd Ed., John Wiley & Sons Inc., New York, pp. 213–306 (1949).
23. Wyman, J. Jr., *Phys. Rev.* **35**, 623 (1930).

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Chemical Damage in Wool

Part III: Effects of Aqueous Chlorine[1]

Wm. H. Houff, C. J. Wills, and R. H. Beaumont

F. C. Huyck & Sons, Kenwood Mills, Rensselaer, N. Y.

Abstract

A study of the wet properties of wool exposed to low concentrations of aqueous chlorine under a variety of conditions is reported. Fiber stress–strain data are presented showing the effects of variations in the concentration of chlorine, pH, temperature, time of exposure, and agitation. Comparisons of cystine-cysteic acid percentages as interpreted from paper chromatograms are presented. Alkali solubilities of chlorine-damaged samples were determined, and their relation to other properties is noted.

Introduction

The action of oxidizing agents on the chemical and physical properties of wool has been widely investigated [8]. The wool damage caused by chlorine at high concentrations is well known, but little is reported on the effects of low concentrations of chlorine, such as are often used on papermakers' felts and in certain shrinkproofing processes. Since the degradative effects of chlorine oxidation are most apparent in wet wool, the changes occurring in the stress–strain properties of wet fibers after mild chlorination were evaluated. Because it is a time-honored method for detecting chlorine damage in wool, the alkali solubility [10] of chlorine-damaged wool was determined. Simultaneously, these chlorine-damaged samples were analyzed for cysteic acid by a paper chromatographic procedure [12].

The results of the investigation point out the sensitivity of wool to chlorine degradation, particularly

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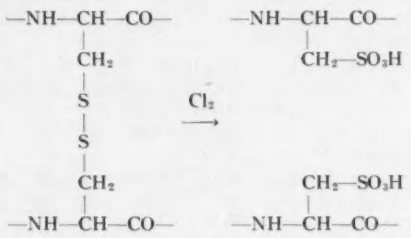
where the fiber must perform for extended periods of time in very dilute chlorine solutions.

Discussion

When an oxidizing agent such as chlorine acts upon wool protein, a primary reaction is rupture of the disulfide bond with conversion of cystine to cysteic acid.



With the exception of tyrosine, other amino acids in wool are but slowly attacked by aqueous chlorine [3].

Harris and Brown [9] and more recently Alexander, Fox, and Hudson [2] demonstrated that the physical properties of wet wool decrease almost linearly with decrease in cystine content. On the other hand, dry fiber properties are but slightly affected until approximately 60% of the cystine is destroyed [2]. In the dry fiber, physical properties depend heavily upon hydrogen bonds and upon "salt links" established by charged centers on the protein chain. However, polar solvents such as water disrupt many of these bonds, leaving the properties of wet wool largely dependent on disulfide cross links.

The reactivity of chlorine with wool depends upon pH, temperature, concentration, and agitation. At a pH of 10 only 25% of the cystine is oxidized [1]. Acidic or neutral solutions containing sufficient chlorine oxidize all the cystine. In addition, the reduction in work in extending the samples 30% was greater in fibers exposed to chlorine solutions buffered at pH 2 than at pH 10. The difference in chlorine reactivity is rationalized readily in terms of the ionic and molecular forms present in aqueous chlorine solutions at various pH values [1].

Most reactions between wool and an aqueous solute are very dependent on the rate of agitation [7]. This is particularly true in dilute solutions of solutes having a small molecular or ionic size [5, 6, 12]. It has been pointed out that the thickness of the diffusion layer about the fiber is, in general, inversely proportional to the rate of stirring [5]. Only at large solute concentrations or high degrees of agitation does the rate of a liquid phase chemical process on wool become independent of stirring rate [4]. Under these conditions the rates of many reactions, including chlorine oxidation, are dependent upon the rate of diffusion through the fiber rather than upon the nature of the chemical reaction, which is comparatively rapid [4].

The present investigation was concerned with determining the effects of aqueous chlorine at high dilution upon the physical and chemical properties of wool under a variety of conditions. The samples, composed of single, pretested, mounted wool fibers and a small quantity of scoured wool, were immersed in a large volume (20–30 l.) of chlorine solution adjusted to the desired concentration, pH, and temperature. Duplicate experiments were run with no mechanical stirring being employed in one solution, while the other was agitated by a high speed pro-

TABLE I. Effect of Aqueous Chlorine on Wool Properties in 24 Hr. at 25° C.

Chlorine conc., p.p.m.	No agitation			With agitation			
	% Retention		Est. cystine converted, %	% Retention		Alkali sol., %	Est. cystine converted, %
	F_y	F_{20}		F_y	F_{20}		
0.0	100	100	0	100	100	5.5	0
0.5	98	98	5	90	90	9.8	5–10
1.0	—	—	—	81	82	15.2	10–20
2.0	94	94	5–10	73	78	22.4	20–25
4.0	88	88	10–20	57	59	—	—
6.0	77	78	20–30	29	31	46.7	50–60
8.0	60	65	25–35				
10.0	52	55	30–45				
15.0	42	47	40–55				
20.0	25	29	45–65				

peller. Additional amounts of chlorine were added to each as periodic analysis indicated reductions in concentration. All physical measurements were made on an Instron tester [11]. The single fiber samples were tested wet to render the effects of disulfide bond rupture more evident and also because the practical application being studied (papermakers' felts) involves wet wool. The amounts of cystine conversion were estimated by paper chromatographic analysis [12] of the amino acids contained in hydrolysates of the samples. Alkali solubility [10], which was presented as a means of assaying chlorine damage in wool, was determined on some of the samples at the same time.

At room temperature (25° C.) and pH 4.5, the changes caused in wool by a 24-hr. exposure to solutions containing between 0.5 and 20 p.p.m. of chlorine were determined. The stress–strain curves of the wet fiber samples before and after exposure were determined. The values at the fiber yield point (Fy) and at 20% extension (F_{20}), converted to percentages of the values for untreated fibers and expressed as percent retention, are presented in Table I.

The effects of agitating the chlorine solution during exposure are very apparent. In fact, in a 24-hr. period a stirred solution at 0.5 p.p.m. chlorine causes approximately the same property loss as an unstirred solution at 4.0 p.p.m. Paper chromatographic analysis of samples showed increasing quantities of cystine-cysteic acid conversion with increase in chlorine concentration. These values correlate closely with the reduction in force value. No changes were noted in the other amino acids found in wool. However, changes in tryptophane would be undetermined, since it is destroyed by acid hydrolysis. At the same time, the quantity of methionine is so small that alteration of this amino acid might go undetected.

Only the samples in the stirred solutions had alkali solubility measurements taken. A regular, gradual increase in these values is noted. However, it should be pointed out that the lack of specificity of alkali solubility could cause misinterpretations where the sample history is poorly defined. Attack by either bacteria or strong acid may cause sizeable increases in alkali solubility. Even the mechanical action of textile processing causes an increase.

An increase in solution temperature from 80° to 120° F. greatly accelerates the action of chlorine. At a pH of 4.5, exposure time of 24 hr., and 6 p.p.m. of chlorine, the changes in wet fiber properties are as illustrated in Figure 1. Only an unstirred system was employed for this study.

The results of varying the pH of the chlorine solution are in agreement with expectations as indicated by the studies of Alexander, Hudson, and Fox [1]. The amount of cysteic acid formed at pH 8 or higher was much less than in more acidic solutions. Likewise, the effect on wet fiber properties was less unless the pH was increased to 10.5 or more; then the basic solution caused cystine-to-lanthionine conversion with accompanying property loss. In Figure 2 are plotted the percent loss in yield force vs. pH for wet fibers exposed to three unstirred solutions containing 6 p.p.m. of chlorine at varying pH. Because of the greater reaction rate, a chlorine concentration

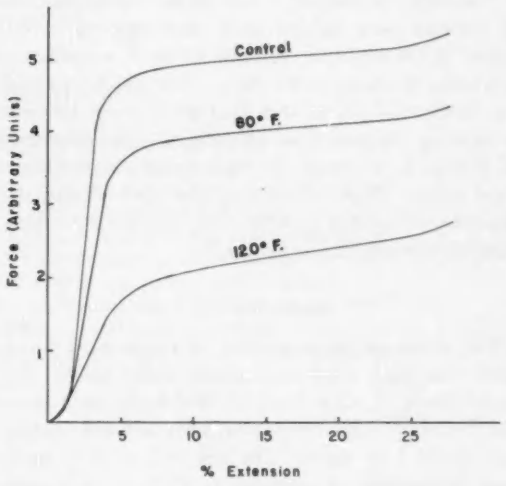


Fig. 1.

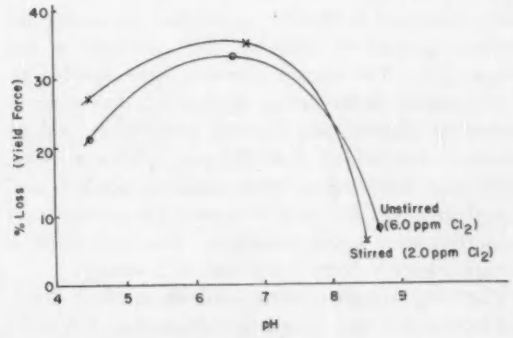


Fig. 2.

TABLE II. Effects of Solution pH on Wool Chlorination

	6.0 p.p.m. (no agitation)	2.0 p.p.m. (with agitation)	
pH	Est. cystine converted, %	Est. cystine converted, %	Alkali solubility, %
4.5	20–30	20–30	22.4
6.8	25–35	25–35	24.5
8.5	5	5	7.4

of 2.0 p.p.m. was used in the stirred solution. In Table II the results of paper chromatographic analysis and alkali solubility measurements are summarized. These results are closely related to the changes in the stress–strain properties of the single fiber.

The more prolonged action of low concentrations of chlorine was studied at a concentration of 6.0 p.p.m. in the unstirred solution at room temperature and times of one to seven days. The stirred solution was held at 2.0 p.p.m. with four days being sufficient to destroy the wet fiber properties. As illustrated in Figure 3, a steady decrease occurs in wet fiber yield point. Paper chromatograms showed that the amounts of cystine-cysteic acid conversion closely parallels the physical property loss.

Experimental

The stress–strain properties of single wool fibers were measured using an Instron tester [11]. Selected fibers of New Zealand 44's fleece wool were mounted with Duco cement between cellulose acetate tabs placed 1 in. apart. The wet properties of these were determined by extension to 25% of the sample length in a pH 6.7 buffer at a head travel of ½ in./min.

The pretested fibers and 0.5–2.5 g. of loose wool were immersed in 20–30 l. of solution containing the desired amount of chlorine and buffered to the proper pH. The stirred solutions were agitated by a high-speed motor-driven propeller. The concentration of chlorine was checked periodically and its variation was held at ± 0.25 p.p.m. After a 24-hr. immersion the samples were removed, washed, and placed in a pH 6.7 buffer, where the stress–strain properties were again measured. For each solution variation twelve fibers were used as a sample.

The 0.5-g. sample of loose wool was washed, dried, and hydrolyzed in a sealed tube containing 6 *N* HCl at a temperature of 125° C. for 5 hr. Using a previously described method [12], the amino acids were examined on two-dimensional paper chromatograms. The quantities of cystine and cysteic acid were estimated by comparison with chromatograms of amino acid solutions containing known amounts of cystine and cysteic acid.

Alkali solubility measurements were made on samples of 1.0 ± 0.1 g., according to the previously described procedure [10].

Summary

From the data presented it is concluded (1) that very low concentrations of aqueous chlorine seriously decrease the usefulness of wet wool fibers under conditions similar to those found in many papermaking and bleaching operations; (2) that the amount of cystine converted to cysteic acid is closely related to the decrease in stress–strain properties of the wet fiber; (3) that the rate of degradation is accelerated by small temperature increases; (4) that degradation increases to a maximum at approximately neutral pH and then drops off rapidly at a pH of 8.5–8.7; (5) that under a given set of conditions the amount of degradation progresses with time until wet fiber utility disappears; and (6) that the rate of chlorine attack is many times greater where heavy agitation is used.

Acknowledgment

The authors wish to acknowledge the assistance of C. D. Rawlings in checking and maintaining chlorine concentrations. They are also indebted to George Lehner, who prepared the paper chromatograms.

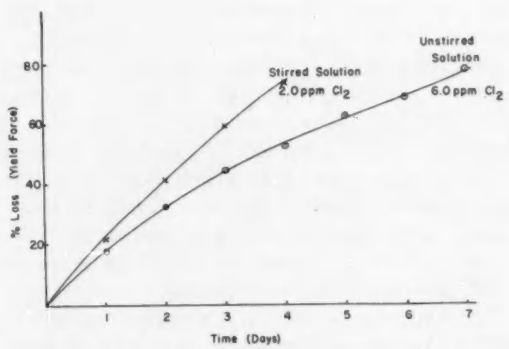


Fig. 3.

Literature Cited

1. Alexander, P., Fox, M., and Hudson, R. F., *Biochem J.* **46**, *27* (1950).
2. Alexander, P., Fox, M., and Hudson, R. F., *Ibid.* **49**, 129 (1951).
3. Alexander, P. and Gough, D. M., *Ibid.* **48**, 504 (1951).
4. Alexander, P., Gough, D., and Hudson, R. F., *Trans. Faraday Soc.* **45**, 1109 (1949).
5. Alexander, P., Gough, D., and Hudson, R. F., *Ibid.* **45**, 1058 (1949).
6. Alexander, P. and Hudson, R. F., TEXTILE RESEARCH JOURNAL **20**, 481 (1950).
7. Alexander, P. and Hudson, R. F., "Wool, Its Chemistry and Physics," Chapman and Hall, Ltd., London, England, pp. 153–156 (1954).
8. Alexander, P. and Hudson, R. F., *Ibid.*, pp. 260–278.
9. Harris, M. and Brown, A. E., *Symp. Fibrous Proteins*, 203 (1946).
10. Harris, M. and Smith, A. L., *Am. Dyestuff Reptr* **25**, 542 (1936).
11. Hindman, H. and Burr, G. S., *Trans. Am. Soc. Mech. Eng.* **71**, 789 (1949).
12. Houff, W. H. and Beaumont, R. H., TEXTILE RESEARCH JOURNAL **26**, 871 (1956).
13. Hudson, R. F., *Discussions Faraday Soc.* **12**, 15 (1954).

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Parachute Engineering

The University of Minnesota has been selected by the committee of the Department of Defense on parachute engineering education to conduct a short course in Parachute Engineering and Retardation July 14–25, 1958 under the direction of Dr. Helmut G. Heinrich, professor in the department of Aeronautical Engineering and project scientist on joint Army, Navy, and Air Force basic research on parachute and other retardation devices. The course will be arranged to acquaint representatives of the armed services. research institutions, and industry with a status of aerodynamic retardation. Besides lectures, demonstrations in the subsonic, supersonic, and water analogy facilities on research objectives of aerodynamic retardation and field trips to local industrial research facilities are planned. Lectures will be given by University of Minnesota staff and guest lecturers from other educational institutions, Department of Defense, and industry.

INDUSTRIAL SECTION

Physical Properties of Fibers and Yarns of Partially Acetylated Cottons

Rollin S. Orr, Louis C. Weiss, Albert W. Burgis, and James N. Grant

Southern Regional Research Laboratory,[1] New Orleans, Louisiana

Abstract

Samples of cotton of Deltapine, Rowden, and Stoneville varieties were partially acetylated as bulk cotton and as untreated 14/3 yarns to acetyl contents ranging from 9 to 26%. Breaking loads and elongations at break of single fibers, fiber bundles, and yarns were decreased by the partial acetylation up to about 17%, but showed a tendency to increase above 20% acetyl content. Moisture conditions have less effect on tenacity of yarns of 25% than on those with lower acetyl content. Tenacities of the acetylated yarns when wet were slightly lower, and when desiccator-dried were higher than those of the untreated controls. Below 15%, the relation of density to acetyl content was consistent with calculations based on the preferential reaction of amorphous cellulose in the initial stages of the reaction. Resistance to heat degradation increased with acetyl content up to 25% acetyl. The pH of the water used to rinse the reacted yarns was an important factor influencing heat degradation. Maximum retention of strength occurred when the wash water was in the pH range of 10–11. A slight but consistent difference in heat resistance of the partially acetylated cottons was associated with different varieties.

THE partial acetylation of cotton has been found to produce a modified cellulose with improved resistance to chemical and heat degradation [4, 14] and to microbiological deterioration [6, 8, 25]. While the general appearances of the fiber and its products are essentially unchanged from that of scoured cotton, significant changes are found in the physical properties of the fibers [2, 4, 13, 14, 16]. These changes were shown to be related both to inherent characteristics of the cotton and to the extent of chemical substitution [4, 14, 16, 17, 23, 24].

In a previous investigation of the fiber properties of partially acetylated cottons (PA cottons) [16] the degree of substitution was limited to a narrow range, averaging about 24% acetyl. The reactions were carried out with the yarns held under sufficient tension while in the acetylating solution to prevent a contraction in length. Partial acetylation within the range of 22–26% has been found to produce textile products with excellent heat and rot resistance. However, several properties of the fibers and yarns, such as low elongation and processing characteristics, appeared undesirable for certain textile uses. In an attempt to define more fully the factors responsible for these undesirable fiber properties and to seek conditions for partial acetylation with greater potentialities for producing satisfactory textile fibers,

[1] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, United States Department of Agriculture.

partially acetylated cotton was produced with acetyl contents ranging from 8–26%. The reaction was carried out on unprocessed cotton fibers and on yarns processed from them which were allowed to shrink during treatment.

Samples

Samples of unpurified cotton of Deltapine 15, Rowden 41B, and Stoneville 2B varieties were chosen for partial acetylation because, in previous investigations [16], cottons of these varieties had differed in their response to the treatment. The samples chosen are not necessarily representative for the entire variety. Samples of the cottons were in the form of unprocessed cotton fibers and 3-ply yarns. Yarn constructions were 14:Z 11/3:S 6.5 turns/in. (tpi) (3.0 twist multiplier, TM) for low twist yarns; 14:Z 15.3/3:S 8.9 tpi (4.1 TM) for medium twist yarns. Deltapine and Rowden were processed into yarns of both twists and Stoneville into only the medium twist.

Fiber samples for single fiber tests were obtained from yarns and unprocessed stock by combining the modal and two adjacent length groups of the length array.

Experimental Procedure

Treatment

Portions of the unscoured cotton were partially acetylated both as fibers and as yarns in a laboratory apparatus by the method developed at this laboratory [5, 8, 9]. The acetyl contents were varied by controlling the length of reaction time. For the lowest degrees of substitution, the reaction time was about 30 min.; for the highest degrees of substitution, the time was more than 1 hr. In these studies the yarns and fibers were allowed to contract in length during the reaction. After the reaction, the fibers and yarns were washed in tap water (pH 9–10).

Test Methods

All samples were conditioned in standard atmosphere (70° F., 65% R.H.) for 3 da. before measuring the properties which are influenced by moisture. Atmospheric conditions of tests designed to show effects of moisture are given in the discussion of the results. Samples of the unacetylated and PA cottons were heat degraded at 160° C. for periods ranging from 2–8 da. These were the times, determined from preliminary studies, required to produce losses in tenacity of desired amounts.

Fiber lengths and moisture regain measurements were made according to ASTM recommended procedures [1*a*, 1*b*].

Tensile tests were made on single fibers taken from the composited length groups [10] with the TRI-Schaevitz [2] electronic tester [22]. The rate of strain

[2] The mention of trade names does not imply their endorsement by the Department of Agriculture over similar products not mentioned.

TABLE I. Physical Properties of Unacetylated and Partially Acetylated Cotton Fibers

					Single fiber*		Bundle	
	Acetyl, %	Moisture content, %	Fiber length, mean, in.	Linear density, grex†	Tenacity, g./grex††	Elong. at break, %	Tenacity,** g./grex††	Elong. at break,*** %
Deltapine	0.0	6.3	1.06	1.89	2.8	10.5	2.1	11.0
	15.4	4.6	.97	2.20	2.0	8.8	1.6	8.2
	20.5	4.1	1.00	2.23	2.0	9.2	1.6	8.3
Rowden	0.0	6.3	.90	2.62	2.4	8.8	2.0	9.1
	13.9	4.8	.86	2.81	1.9	7.4	1.7	7.4
	22.3	3.9	.85	3.01	1.8	7.4	1.6	7.4
Stoneville	0.0	6.3	.86	1.91	2.2	7.6	1.8	8.0
	14.1	4.7	.76	2.07	1.6	5.9	1.6	6.9
	21.9	4.0	.79	2.15	1.6	6.1	1.4	6.1

* Length of specimen tested 7.5 mm.
** Width of jaw spacing 2.5 mm.
*** Bundle elongation measured with 2.5 mm. jaw spacing.
† Multiply by 0.1 to convert to tex.
†† Multiply by 10 to convert to g./tex.

was about 50% elongation/min.; thus, about 12 sec. was required to break an average single fiber. Tensile tests were made on at least 100 fibers of each sample.

In preparation of cottons for bundle tests, the fibers were combed to increase their alignment according to the techniques described for bundle tests [18]. Before heat degrading fibers for bundle tests, the fibers were removed from the combs and confined between porous paper. Bundle tenacity and elongation at break measurements were made with the Stelometer [2] at clamp spacings of 0, 1, and 2.5 mm., or, in special tests, at the clamp spacings indicated. Rate of loading was controlled at 0.5 kg./sec. and breaking loads of all bundles were kept near 4 kg. The time required for break was about 8 sec., which was comparable to the time required to break the single fibers.

Tensile tests were made with the TRI-Schaevitz electronic tester on 20 specimens of yarn at a gauge length of 10 in. The rate of strain was 20%/min.

Results and Discussion

Table I gives for each of the three varieties the results of both single fiber and bundle measurements made on unprocessed cotton fibers before acetylation and after acetylations to two different levels of substitution. Table II gives the tenacities and elongations of the fiber bundles from the defibered unacetylated yarns, and the breaking loads and elongations of yarns of the two twists. Measurements given in these two tables have been used to calculate the percentage change caused by the acetylation and by heat degradation.

TABLE II. Tensile Properties of Unacetylated 14/3 Yarns and Fibers Taken from Them

	Fiber bundles*		Yarns		
Sample	Tenacity, g./grex**	Break elong., %	Ply twist, tpi.	Break load, g.	Break elong., %
Deltapine	2.16	10.5	6.5	2140	8.0
	2.12	12.0	8.9	2340	9.4
Rowden	2.18	9.3	6.5	1890	7.1
	2.09	8.7	8.9	2130	8.6
Stoneville	1.80	10.0	8.9	1950	7.8

* Bundle tenacity and elongation measured with 2.5 mm. jaw spacing.

** Multiply by 10 to convert to g./tex.

Effects of Partial Acetylation on Tensile Properties

When comparing tensile properties of cottons for effects of acetylation, fiber and yarn swelling, increases in weight, and changes in surfaces of the fibers must be considered. While trends found from tensile properties of fibers, fiber bundles, and yarns lead to similar conclusions, the breaking loads of single fibers have been considered as the measurement which is least affected by changes in other properties. Single fiber tensile measurements are considered more reliable than those of bundles or yarns for prediction of molecular rearrangement in the partial acetylation of cottons.

The upper half of Figure 1 gives the breaking loads of acetylated single fibers expressed as percentages of the unacetylated fibers. The curve drawn represents an average trend for the three samples. The percentage breaking load retained by the yarns was slightly greater than that of the fibers. This is in agreement with observations by McDonald et al. [16] on fibers from yarns which were acetylated while held at their original length.

In the lower half of Figure 1, the elongations at break of the single fibers follow a pattern similar to that of their breaking loads.

If the tensile properties are expressed as tenacity (g./grex), the percentage decrease due to acetylation is greater than that of breaking load. A tenacity adjusted for change in linear density caused by loss of moisture and gain in acetyl groups is more nearly equivalent to breaking load than to unadjusted tenacity.

In Figure 2 are given the adjusted cellulose tenacities of bundles of fibers for the three cottons which were acetylated in the yarns. These tenacities were adjusted by dividing the measured values by $(1 - .01\ M)\ (1 - .01\ A)$ where M is the moisture content and A is the percent by weight of added acetyl groups. The smooth curve drawn through the observations indicates again that the decrease in cellulose tenacity follows the trend found in breaking loads of fibers and yarns. Even though differences in the percentages of retained strengths were observed among the fibers, fiber bundles, and yarns, the greatest losses in strength usually occur near the 17% acetyl content.

A possible explanation for the increases in breaking loads, elongations at break, and tenacities above the 17% acetyl content may be found in the uniformity of acetylation along the fiber as acetyl con-

tent is increased above that value. Such nonuniformity as shown by the dye and microscopical tests [5, 26] indicates that the degree of acetylation, while apparently uniform from the center to the circumference of the fiber, was nonuniform along the length. A lack of uniformity of acetylation in any cross section of fibers, in either bundles or yarn, would increase the variation in elongation at break, thereby reducing bundle or yarn efficiency [21]. The explanation for bundles does not explain a similar minimum elongation and strength for single fibers (Figure 1).

An alternate explanation may be found in the heterogeneous nature of the acetylation reaction. It is well established that the acetylation reaction begins with the more accessible disordered (amorphous) regions, converting these to the triacetate before the larger crystalline areas are reacted [7, 11, 12]. Increases in breaking load and elongation of fibers above an acetyl content of 17% possibly result from the breaking up of smaller crystallites and subsequent release of strain within the fiber. This explanation of increase in strength by removal of strain also is proposed often as a factor responsible for increase in strength by wetting of untreated cotton [3].

Effects of Moisture on Tensile Properties

Further evidence that acetylation may change the tensile properties by tying up hydrogen bonding sites, which otherwise would serve as sites for adsorbed moisture, is shown by the dependence of bundle tenacity on relative humidity. Figure 3 gives average tenacities and elongations at break of the three cottons at 70° F. with relative humidities of 65% and 81%. Differences in tenacity become smaller at higher acetyl contents where differences in moisture contents are smaller. It can be seen that PA cotton with 16% acetyl at 81% R.H. where the moisture content is 7.20% had a cellulose tenacity comparable to that of the unacetylated cotton at 65% R.H. where the moisture content is 6.8%. While cellulose tenacity was essentially equal at comparable moisture contents the elongation at break of the PA cotton at 81% R.H. was higher than that of the unacetylated cotton at 65% R.H.

In Figure 4 are shown the effects of moisture on breaking loads and elongations of yarns of several acetyl contents. While breaking loads of yarns when tested at standard conditions were essentially unchanged by the acetylation, breaking loads of wet yarns decreased, and those of desiccator-dried yarns increased with increases in acetylation; the desiccator-dried yarns had less than 1% moisture content. At the highest acetyl content, 26%, moisture had very little effect on breaking load. It is possible

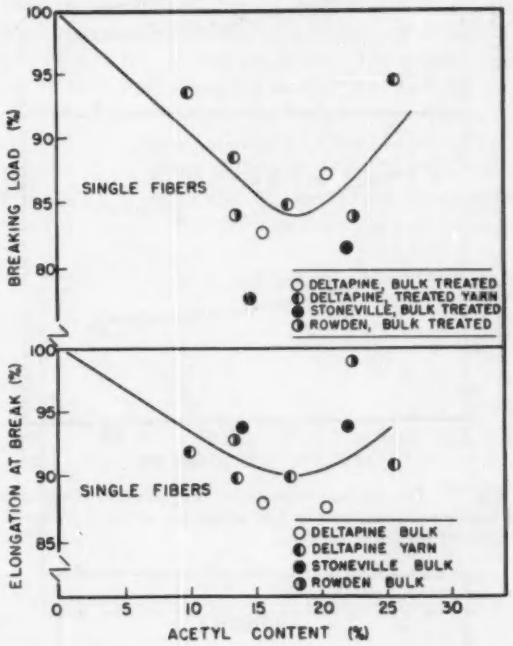

Fig. 1. Relation of percent breaking load and elongation at break retained to the acetyl contents for single fibers.

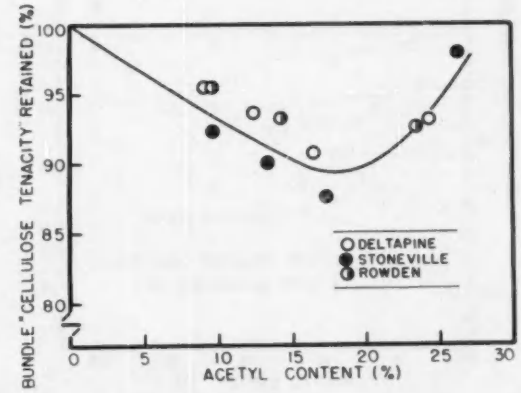

Fig. 2. The relation of bundle cellulose tenacity retained to the acetyl contents for Deltapine, Stoneville, and Rowden cottons.

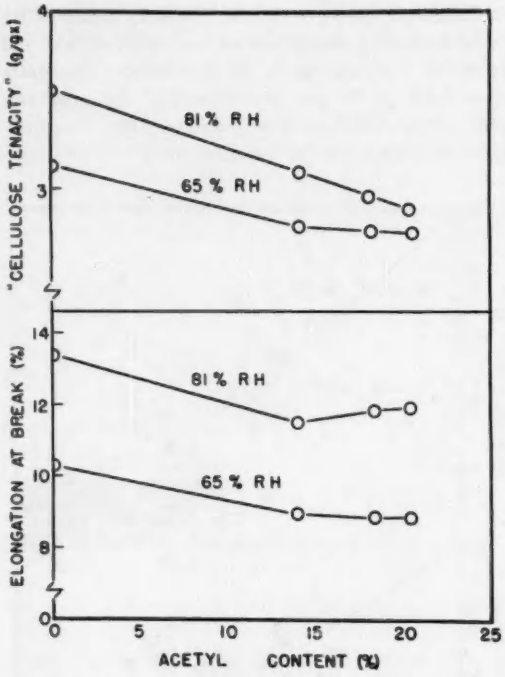

Fig. 3. The average relation at two moisture conditions of bundle cellulose tenacity and elongation at break to acetyl content of the three cottons.

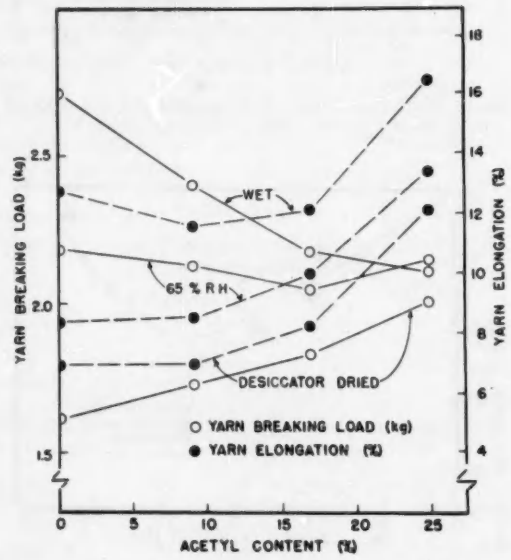

Fig. 4. The relations of yarn breaking load and elongation to acetyl content at the three moisture conditions, averages for the three cottons.

that these changes are effected by breaking of primary bonds by hydrolysis during the acetylation reaction as well as by tying up hydrogen bonding sites. Elongation, however, was increased both by the absorption of moisture and by the swelling reaction. Figure 3 also indicates that moisture increases the elongation of acetylated less than it does the unacetylated yarns. An increase of elongation was expected for yarns which were treated while relaxed, since the fibers are more highly swollen during such treatment than when held at constant length [16]. Increases in elongation of yarns are experienced also when, in the process of scouring, fibers are swollen by much milder swelling agents, such as water.

Elastic Recovery

The elastic recovery of the acetylated cottons was measured from the elongation of fibers at the specified rate when loaded to 2.5 g. (approximately 50% of the average breaking load), relieved of the load at the same rate, and immediately reloaded in order to secure a second and complete load–elongation curve for the fiber. In Table III are given the average elongations at 2.5 g. as measured from 0.1 g. initial load from both the first and second loadings, as well as the ratios of these elongations for each of the bulk acetylated cottons. The elongations of the acetylated cottons were consistently lower than those of the unacetylated except for the second loadings of the Stoneville and Rowden of the highest acetyl contents. However, the ratios of the elongations of the second to the first loading increased with acetylation. These increased ratios indicate an increase in the ability of the acetylated fiber to recover after having been tensioned. The lower elongation of the acetylated at 2.5 g. load as compared to unacetylated shows that there is an increase in the secant modulus (average stiffness). Since secant modulus is expressed as g./grex/elong., which considers the total mass of the fiber rather than the mass of cellulose, the increase is small because of the small mass added in acetylation.

Density

Evidence that the amorphous portions of the fiber are acetylated first is shown by the curvilinear relation of density to acetyl contents below 15%, shown in Figure 5. In earlier investigations [20], the rela-

tionship of density to acetyl content was shown to be approximately linear between 15 and 46% acetyl. Density measurements of cotton of less than 15% acetyl content agree satisfactorily with the densities calculated if a heterogeneous state is assumed. In calculations of these densities, the assumption was made that unacetylated cotton was composed of 20% amorphous and 80% crystalline cellulose. Also, the assumptions were made that the amorphous cellulose had an average density of 1.48 g./cc., or 0.02 g./cc. less than that of ball-milled cellulose, and the crystalline part had a density of 1.57 g./cc., or about 0.02 g./cc. less than that of pure crystalline cellulose I as calculated from the X-ray pattern. The process of acetylation was assumed to follow the generally accepted theory of reaction, which is the production of triacetate from the amorphous cellulose (density 1.32 g./cc.), proceeding into the crystalline region after the amorphous has been reacted [11].

Heat Degradation of Acetylated Cotton

Earlier studies of degradation of untreated fibers and yarns by heat showed single fibers to lose strength more rapidly than do yarns [19]. Differences in rates of loss have been accounted for in part by the deleterious effects of contact of fibers with the hands during the defibering of yarns and sorting the fibers into length distributions prior to heating. These studies have shown that washing the fibers and yarns of unacetylated cottons with water or alcohol prior to heating decreases their rates of degradation; others have shown that the pH of the wash water has a pronounced effect upon the rate of heat degradation of untreated cotton [15]. The effects on heat degradation of rinsing in water with pH ranging from 2.8 to 11 were determined on unacetylated and bulk acetylated cotton and the yarns of 20% acetyl content. Rinse water of either low or high pH was obtained by adding to distilled water either HCl or NaOH. Samples were soaked with agitation for 30 min., the excess liquid was removed, and the samples air dried. The unacetylated yarns were heat degraded at 160° C. for 2 da. and the PA yarns for 7 da. In Figure 6 are shown the relations of retained tenacities to the pH of the rinse water. Both yarns (Curves *A* and *B*) and fiber bundles (Curves *C* and *D*) show that the strength retained after heating increases with pH of the rinse

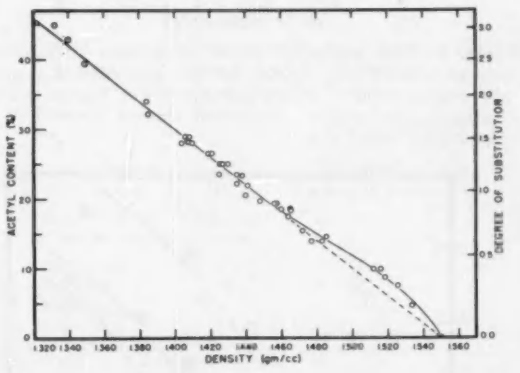

Fig. 5. The relation between acetyl content and density of partially acetylated cottons.

TABLE III. First and Second Elongation of Bulk Acetylated Fibers at 2.5 g. Load and Ratio of Second to First

Sample	Acetyl, %	Elongation at 2.5 g.* First loading Mean, %	First loading C.V., %	Second loading Mean, %	Second loading C.V., %	Ratio second to first loading, %
Deltapine	00.0	5.8	43	2.2	23	38
	15.4	3.8	40	1.6	26	45
	20.5	3.8	40	1.7	25	46
Rowden	00.0	3.7	45	1.8	27	50
	13.9	3.3	49	1.7	28	50
	22.5	2.7	39	1.8	25	67
Stoneville	00.0	4.9	41	2.1	24	43
	14.1	3.1	48	1.6	28	51
	21.9	3.3	41	2.2	22	68

* Elongations measured from 0.1 g. load.

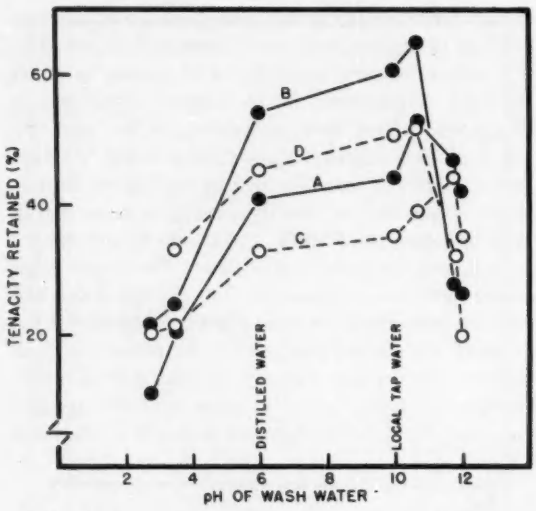

Fig. 6. The relation of pH of rinse water to percent tenacity retained after heating for (*A*) unacetylated yarns, (*B*) acetylated yarns, (*C*) unacetylated fiber bundles, (*D*) acetylated fiber bundles. Acetylated samples heated 7 da., unacetylated heated 2 da.

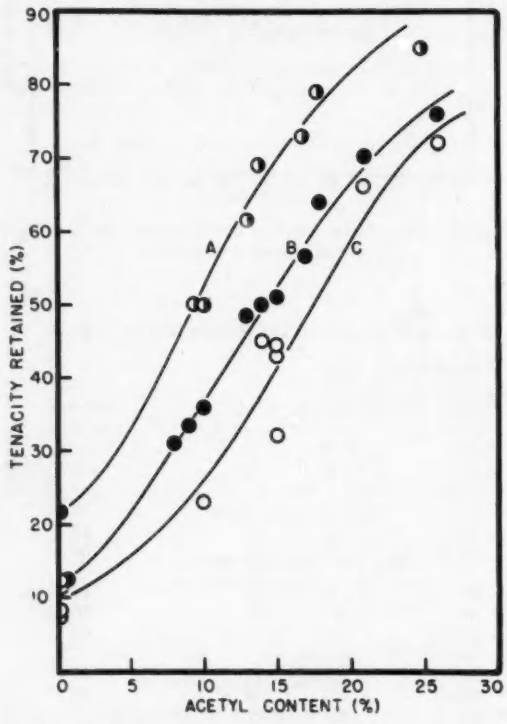

Fig. 7. The relations of tenacities retained to the acetyl contents for (*A*) yarns, (*B*) bundles, and (*C*) single fibers of Deltapine cotton after heating for 4 da. at 160° C.

water up to about pH 11. A further increase to pH 12 causes a sharp decrease in heat resistance of acetylated cotton, but only a slight decrease in that of the unacetylated. Since strength retention reached a maximum when materials were rinsed in water with pH about that of the local tap water (pH 10), a regular procedure was adopted of rinsing samples in tap water before heat degrading. The chemicals used to produce the rinse water of different pH values and the procedure followed in producing partially acetylated cotton could have effects on the heat resistance of the material.

The relation of tenacities after heat degrading to acetyl contents for single fibers, fiber bundles, and yarns of Deltapine cotton are given in Figure 7. The curves show that protection from heat degradation increased with increasing acetyl contents; i.e., with decreasing free hydroxyl groups. The protection increases rapidly above 10% acetyl content, and appears to level off above 25%, when all but the most inaccessible crystalline part is considered to be acetylated. While the percent tenacity retained for a given acetyl content was different in fibers, bundles, and yarns, the trends were similar by each method used to measure the heat resistance.

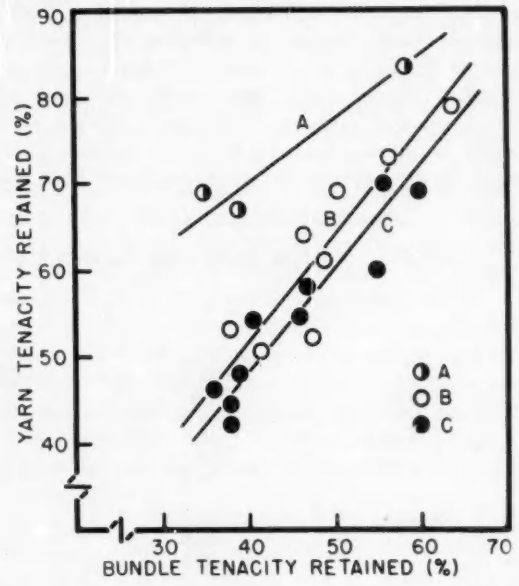

Fig. 8. The relation of tenacities retained by the yarns to that of the bundles after heating at 160° C. Curve *A*, acetyl contents 20–26%, heated 7 da.; Curve *B*, acetyl contents of 10–20%, heated 4 da.; Curve *C*, acetyl contents 0–10%, heated 2 da. Deltapine, Rowden, and Stoneville cottons.

In Table IV are given the percentages of tenacity retained at 13.8 and 25% acetyl contents as extrapolated from the curves of bundle and yarn tenacity retained at different acetyl contents of the three different cottons. The lowest percentages of retained tenacity at both acetyl contents were found for the Rowden and the highest for the Deltapine cotton.

In Figure 8 are given the relation of yarn to bundle tenacity retained by the cottons of several different levels of acetyl content after heating at 160° C. for different periods of time. The greatest differences between the tenacities retained by the yarns and the fibers were associated with the higher acetyl contents (greater than 20%, Curve *A*), which were heated 7 da.

Differences in the percentage tenacity retained upon heating by fibers, bundles, and yarns (Figure 7) are not explainable by the protective action against heat and moisture of surface fibers in yarns, since fibers heated within a mass of fibers showed strength losses equivalent to those of the unprotected fibers in small bundles. However, one explanation for differences between rates of losses of tenacity in fibers and yarns may be associated with decreases in tenacity that occur with increases in test length of specimen. The drop in tenacity as gauge length is increased is a measure of the uniformity of breaking load along the fiber. The fact that the bundle tenacity of heated samples decreases more than unheated as jaw spacing is increased from 0 to 2.5 mm. indicates that heating decreases the uniformity of strength along the fiber length (Table V). Since strength of fibers, fiber bundles, and yarns was not measured on equal lengths of specimen, the "effective gauge length" for fibers in a yarn can reasonably be assumed to be less than that of a bundle at 2.5 mm. jaw spacing, and perhaps nearer to that of bundles at 0 spacing. Losses in tenacity would then be greater on the bundles at the 2.5 mm. spacing than on the yarns, as seen in Figure 7. Also, another study has shown that "effective slip length" in bundles varies inversely with frictional forces between fibers and is proportional to the fiber tenacity [18]. Any increase in friction brought about by heating would reduce this effective slip length of fibers in yarns and reduce the observed tenacity loss caused by heating. Since the single fibers were tested at the longest gauge length (7.5 mm.), their losses would be greater than those of the fiber bundles or the yarns.

TABLE IV. Percentages of Tenacity Retained after Heating Partially Acetylated Samples of Deltapine, Stoneville, and Rowden Varieties

Sample	Tenacity retained, %	
	Bundles	Yarns
Acetyl content 13.8%, period of heating 4 da.		
Deltapine	50	69
Stoneville	46	62
Rowden	40	56
Acetyl content 25.0%, period of heating 7 da.		
Deltapine	54	79
Stoneville	45	73
Rowden	41	69

TABLE V. Bundle Tenacities of Unheated and Heat Degraded Fibers Taken from Acetylated Rowden Yarns

Acetyl, %	Heating period, da.	Tenacity				
		0 mm. spacer		2.5 mm. spacer		
		Average, g./gx.*	Decrease with heating, %	Average, g./gx.*	Decrease with heating, %	Decrease, 0 to 2.5 mm. spacer, %
0	0	3.20	—	1.88	—	41
8	0	3.09	—	1.79	—	42
22	0	2.43	—	1.30	—	46
24	0	2.53	—	1.43	—	44
0	1	1.77	45	.83	56	53
8	2	1.75	43	.94	48	46
22	2	1.83	25	.94	28	49
24	2	1.90	25	.97	32	49

* Multiply by 10 to convert to g./tex.

Bundle tenacities of extremely degraded fibers (Figure 7) are probably biased upward by the greater ease of breakage and removal of fibers during preparation of bundles.

Summary

Breaking loads of single fibers, fiber bundles, and yarns were decreased by partial acetylation, reaching a minimum at approximately 17% acetyl, then increasing slightly from the minimum as acetyl contents increased to 26%.

The relationship of density to acetyl content of PA cotton was found to be slightly curvilinear for substitution below 15% but strictly linear above, and in agreement with calculations based on preferential reaction of the amorphous cellulose followed by reaction of the crystalline. The moisture conditions had little effect on breaking loads of yarns of 25% acetyl content. However, the breaking loads of wet yarns of all acetyl contents were lower than those of the unacetylated yarns, while the breaking loads of very dry acetylated yarns were higher than those of the unacetylated.

Measurements of fiber, fiber bundle, and yarn strength indicated that partial acetylation progressively increased heat resistance of cottons up to at least 25% acetyl.

Heat resistance of PA cotton was found to be strongly dependent upon the pH of the water used to rinse the sample prior to heating. Samples rinsed in water of alkalinity pH 10–11, obtained by adding NaOH to distilled water, gave the maximum heat resistance in both PA and unacetylated cottons.

Slight but consistent differences were found in the heat resistance of PA cottons of the Rowden, Stoneville, and Deltapine varieties.

The results indicate that the best heat resistance is to be obtained by acetylation to at least 20% acetyl content, by final rinsing in slightly alkaline water, and by selecting original cottons which give optimum results. As acetylation reduces elongation at break, which is undesirable for certain purposes, selection of samples of originally high elongation at break is desirable.

Acknowledgments

The authors wish to express their appreciation to A. S. Cooper, Jr. and Constance M. Fleming for acetylating and measuring the acetyl contents of the cottons; to Edith A. Honold for furnishing samples of a wide range in acetyl contents; to John J. Brown for having the cottons spun into yarns; to Annie B. Cooper and Dorothy C. Legendre for measuring fiber lengths; and to Betty A. Burrow for assistance in measuring other fiber properties.

Literature Cited

1. ASTM, (*a*) D 1440–55; (*b*) 629–55T., Amer. Soc. Testing Materials, Philadelphia, Pa.
2. Bletzinger, J. C., *Ind. Eng. Chem.* **35**, 474–480 (1943).
3. Brown, K. C., Mann, J. C., and Peirce, F. T., *J. Textile Inst.* **21**, T186–204 (1930).
4. Chippendale, E. J., *J. Soc. Dyers Colourists* **50**, 142–9 (1934).
5. Cooper, A. S., Voorhies, S. T., Jr., Buras, E. M., Jr., and Goldthwait, C. F., *Text. Ind.* **116**, No. 1, 97–102, 194–5 (1952).
6. Doree, C., *Biochem. J.* **14**, 709–14 (1920).
7. Goldthwait, C. F., Buras, E. M. Jr., and Cooper, A. S., TEXTILE RESEARCH JOURNAL **21**, 831–840 (1951).
8. Goldthwait, C. F., McLaren, J., and Voorhies, S. T., Jr., *Textile World* **96**, No. 2, 115–7, 212, 216 (1946).
9. Goldthwait, C. F., Murphy, A. L., Lohmann, I. W., and Smith, H. O., TEXTILE RESEARCH JOURNAL **22**, 540–8 (1952).
10. Grant, J. N., Morlier, O. W., and Scott, J. M., TEXTILE RESEARCH JOURNAL **22**, 682–7 (1952).
11. Happey, F., *J. Textile Inst.* **41**, T381–403 (1950).
12. Heuser, E., Shockley, W., Adams, A., and Grunwald, E. A., *Ind. Eng. Chem.* **40**, 1500–6 (1948).
13. Hind, G. E. L., *J. Soc. Dyers Colourists* **44**, 280–1 (1928).
14. Honold, E., Poynot, J. M., and Cucullu, A. F., TEXTILE RESEARCH JOURNAL **22**, 25–29 (1952).
15. Kleinert, T. N. and Wincor, W., *Textil-Rundschau* **9**, 201–5 (1954).
16. McDonald, A. W., Humphreys, G. C., Orr, R. S., and Grant, J. N., TEXTILE RESEARCH JOURNAL **26**, 646–652 (1956).
17. New, A. A., *Elec. Commun.* **13**, 216–25, 359–79 (1935); **14**, 213–31 (1936).
18. Orr, R. S., Weiss, L. C., and Grant, J. N., TEXTILE RESEARCH JOURNAL **25**, 939–46 (1955).
19. Orr, R. S., Weiss, L. C., Humphreys, G. C., Mares, T., and Grant, J. N., TEXTILE RESEARCH JOURNAL **24**, 399–406 (1954).
20. Orr, R. S., Weiss, L. C., Moore, H. B., and Grant, J. N., TEXTILE RESEARCH JOURNAL **25**, 592–600 (1955).
21. Platt, M. M., Klein, W. G., and Hamburger, W. J., TEXTILE RESEARCH JOURNAL **22**, 641–67 (1952).
22. Reichardt, C. H., Schaevitz, H., and Dillon, J. H., *Rev. Sci. Instr.* **20**, 509–16 (1949).

23. Schrieber, W. T., Bullock, A. L., and Ward, W. L., TEXTILE RESEARCH JOURNAL **24**, 819–22 (1954).
24. Taylor, J. L. and Owens, E. D., TEXTILE RESEARCH JOURNAL **24**, 810–19 (1954).
25. Thaysen, A. C., Bunker, H. J., Butlin, K. R., and Williams, L. H., *Ann. Appl. Biol.* **26**, 750–81 (1939).
26. Tripp, V. W., Giuffria, R., and deGruy, I., TEXTILE RESEARCH JOURNAL **27**, 14–24 (1957).

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Vapor Phase Method for Preparation of Polyacrylonitrile Coated Cotton Yarn and Physical Properties of the Product

Chester H. Haydel, Hermann J. Janssen, Jeuel F. Seal, Henry L. E. Vix, and Edward A. Gastrock

Southern Regional Research Laboratory,[1] New Orleans, La.

Abstract

Acrylonitrile vapors were polymerized within and upon the individual fiber surfaces of scoured cotton yarns to yield coated products having new and interesting properties. The uniformity of the polyacrylonitrile coating is shown in electron micrographs of the fiber surfaces. Breaking strengths were increased appreciably, particularly when the process was applied to prestretched yarns. High frictional characteristics were exhibited when one coated yarn was pulled against another. Excellent resistance to rot and flat abrasion was obtained in conjunction with a relatively minor improvement in resistance to acid degradation. No essential change in heat and weather resistance was noted. Resistance to flexing, however, was adversely affected by the presence of the polyacrylonitrile.

These polymer coated yarns can be prepared with essentially the same equipment and procedures as required for the vapor phase cyanoethylation of cotton; the only exception is that a different catalyst is employed. This illustrates the utility of acrylonitrile for preparation of a variety of useful cotton products.

Introduction

The polymerization of acrylonitrile within and upon the surfaces of textile fibers to improve their physical and chemical properties has been investigated recently. The deposition of polyacrylonitrile in wool by the ferrous ion-hydrogen peroxide technique [7] was discussed by Valentine in one publication [13] and the evaluation of the product in another [14]. He reported that deposition of 20% by weight of polymer imparted increased resistance to milling shrinkage, flat abrasion, and chemical attack, and also increased the breaking strength without impairing the elastic properties. However, the polymer was deposited as a powdery or granular solid with little or no adhesive properties and was easily removed from the surfaces of the wool fibers.

More recently, Gottlieb reported in a note [5] and in an article with Jeffries [6] that the coating of cotton with polyacrylonitrile improved the rot resistance in a manner comparable to cyanoethylation.

The procedures employed by these workers involved liquid phase reactions. The present paper reports results of a preliminary investigation of a vapor phase procedure for the formation of the polymer coating and of the subsequent evaluation of the coated products. The polymerization was

[1] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

achieved by applying acrylonitrile vapors to cotton yarns which had been previously padded with a dilute solution of a suitable catalyst. In contrast to the wool coatings, this surface coating was found to be strongly bound to the cotton fibers.

Equipment

The vapor phase reactor and auxiliary process equipment are shown in Figure 1. The reactor was constructed of a 1-in. jacketed stainless steel pipe with provisions for measurement and control of temperature, measurement of pressure, and passage of reagent vapors. The connections with the reagent boiler were located near each end of the reaction tube to provide uniform distribution of the vapors. As illustrated, one end of the reaction tube was flange fitted to achieve a vapor-tight seal which could be easily and quickly opened at the conclusion of each experiment.

The boiler received the necessary heat for vaporization of the acrylonitrile reagent from a surrounding thermostatically controlled water bath. Hot water was also circulated continuously through the reaction tube jacket to prevent condensation of reagent vapors on the inside of the tube. The vapor and hot water lines were carefully insulated to prevent excessive heat loss. A high vacuum pump was provided to effect removal of the air in the reaction chamber and thereby obtain greater concentrations of the reagent vapors during the reaction period. Two traps, one containing concentrated sulfuric acid and the other cooled by dry ice, protected the vacuum pump from both moisture and vapors of the reagent.

Procedure

The water bath surrounding the reagent boiler was brought to 80° C. and hot water circulated through the reactor jacket. A 40-yd. skein of 14s/2 equivalent to 42s × 2 tex) Deltapine cotton yarn was immersed for 2 min. in a 0.4% aqueous solution of potassium persulfate catalyst containing 0.1% of Tergitol P-28 [2] wetting agent. The wetted skein was centrifuged to 80% pickup by weight of the catalyst solution and mounted within the stainless steel screen tube (Figure 1), which was then transferred to the vapor phase reactor. The reactor was closed and evacuated for 30 sec., a period sufficient to reduce the water content of the yarn to approximately 45%. Acrylonitrile vapors at the 80° C. reaction temperature were then permitted to enter

[2] Use of trade names in reporting these tests is not to be interpreted as an endorsement by the Department of Agriculture of these products over similar products of other manufacturers.

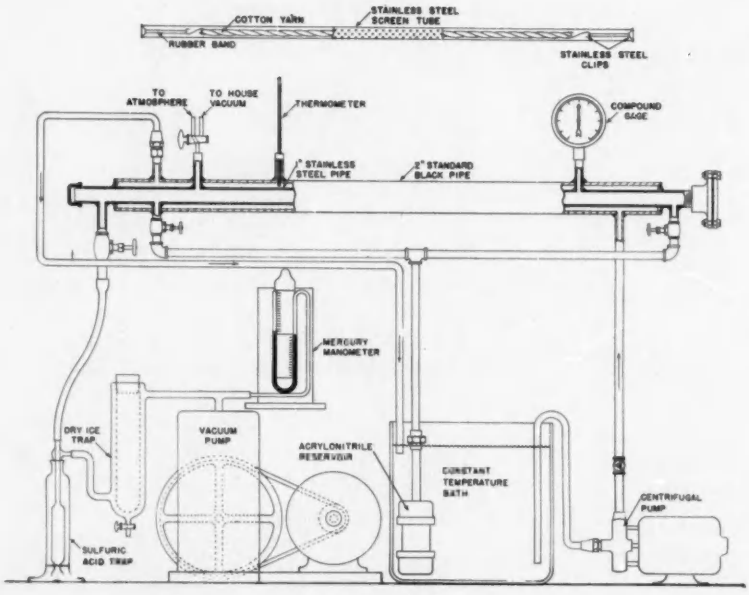


Fig. 1. Apparatus for the polymerization of acrylonitrile vapors within and upon the individual fiber surfaces of cotton yarn.

each end of the reaction tube simultaneously and the reagent allowed to polymerize within and upon the fiber surfaces for a period of 10 min. At the conclusion of this period, the vapors were removed from the reactor unit by alternately applying vacuum and flushing with air. The unit was then opened and the polyacrylonitrile coated yarn was removed from the stainless steel screen tube. This yarn was then washed in water to extract any residual unreacted acrylonitrile and finally dried in a current of cool air. The nitrogen content of the product approximated 5%, which closely corresponds to 19% acrylonitrile polymer.

Microscopical Examination of Products

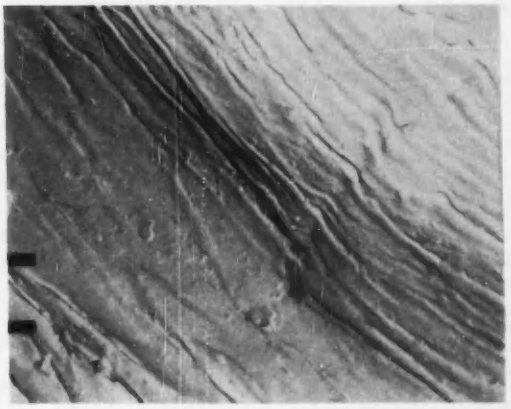
Figure 2 shows electron micrographs of surface replicas of polymer coated raw and scoured fibers from treated yarns and of fibers from a scoured control yarn. The groove pattern of the scoured fiber surface can be distinguished under the polymer coating in the raw cotton sample, but essentially has been obliterated by the coating in the scoured sample. These micrographs also show the better uniformity of the polymer coating over the scoured fiber surface. The occasional very large agglomerates, rarely appearing over the scoured surface, are believed to represent polymerization bridges between adjacent fibers. Such agglomerates are easy to remove mechanically and contribute nothing beneficial. On the basis of these observations the subsequent evaluation was restricted largely to polymer coated scoured yarns.

Results and Discussion of Evaluation Tests

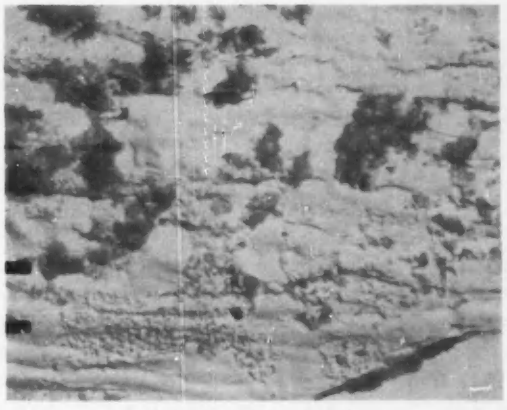
The test results are reported for polyacrylonitrile coated 14s/2 (42s × 2 tex) scoured cotton yarn containing $5 \pm 0.4\%$ of nitrogen, unless otherwise stated. This level of nitrogen was selected after preliminary experiments indicated it to be optimum for improvement of the physical properties. These coated yarns were somewhat stiffened in feel and were white in color. The coating proved remarkably stable to such recommended solvents for polyacrylonitrile as dimethylformamide. Repeated extraction with fresh portions of hot dimethylformamide discolored but did not remove the polymer coating.

Breaking Strength and Elongation

Table I compares the breaking strength and elongation at break of the coated yarn with its scoured con-



Scoured



Raw, polymore coated

Scoured, polymore coated

Fig. 2. Electron micrographs of polyacrylonitrile coated cotton fiber surfaces. Magnification 8000 ×.

TABLE I. Breaking Strength and Elongation at Break of Polyacrylonitrile Coated 14s/2 (42s × 2 tex) Scoured Cotton Yarn and the Effect of Various Pretreatments and Aftertreatments on These Properties

Yarn and treatment	Breaking strength		Elongation, %
	Grams	% of original scoured yarn	
Scoured control	1060	100.0	9.5
Polyacrylonitrile coated	1334	125.9	7.4
Scoured control, stretched dry	1130	106.5	5.1
Scoured control, stretched wet	1110	104.5	4.3
Coated yarn, prestretched dry	1485	140.0	6.1
Coated yarn, prestretched wet	1651	155.9	5.4
Yarn coated under tension, prestretched wet	1713	161.6	3.0
Coated yarn, afterstretched	1410	133.0	6.7
Coated yarn, afterstretched and tempered	1385	130.6	4.4
Coating softened with Triton X-400	1245	117.5	5.7

trol and demonstrates the effect of various pretreatments and aftertreatments upon these properties. The Scott IP-2 tester was employed for these measurements. Formation of the polymer within and upon the fiber surfaces effected a 25% increase in the yarn breaking strength. Since the corresponding increase in linear density approximated only 19%, a slight improvement in tenacity was achieved. This strength increase was accompanied by a small reduction in the elongation at break.

Prestretching treatments at stresses near the yarn breaking strength effected additional increases in the strength of the coated yarns. Wetting the yarn with water prior to stretching was found more effective than a dry stretch. Although the value of wet stretching for larger size yarn has been amply reported previously, particularly in connection with tire cord work [3, 11], the benefit derived for small yarns has usually been negligible. The uncoated yarn was increased only about 5% by wet stretching, whereas the subsequent application of the polymer resulted in a coated yarn of 56% greater strength than the control. Apparently the coating sealed within the yarn those fiber rearrangements or other mechanical changes that occurred during the prestretch. Maximum benefit was derived from application of the coating while the wet yarn was still in the stretched condition.

The deposition of the coating upon the fibers by polymerization of the acrylonitrile vapors would be expected to result in a highly unoriented polymer. Since the tensile strength of synthetic fibers such as Orlon,[3] a drawn polyacrylonitrile, results from the high degree of orientation [8], stretching aftertreatments were employed to enhance this property further in the coated yarns. With the polyacrylonitrile coated yarn, however, the amount of stretch that could be applied was severely limited by the relatively low elongation of the cotton. As a consequence, the amount of orientation achieved in the coating was probably negligible. Nonetheless, aftertreatments which employed a cold stretch effected a small increase in yarn strength. Tempering this stretched coating materially decreased the elongation.

An aftertreatment which involved soaking and working the coated yarn in a 1% aqueous solution of Triton X-400 softener, followed by drying at 100° C., was employed to reduce the stiffness. This aftertreatment improved the hand of the yarn without causing any appreciable loss of strength.

Abrasion and Frictional Properties

In Table II are listed data for the flex abrasion [1*a*], flat abrasion, and frictional characteristics of the polymer coated yarn and its scoured control. The sharply reduced resistance to flexing exhibited by the coated yarn probably reflected the stiffness of the coating. Surprisingly, use of the Triton X-400 softener did not improve this property.

The resistance of the yarns to flat abrasion was measured by a method specifically developed for this purpose. Monolayer bands of yarn were wound on an appearance board, taking care to provide equal tension in each strand, until a 1-in. wide band of 20 thread ends was obtained. The yarns in each finished band were fastened with masking tape. These bands were then abraded on the Wyzenbeek "oscillatory cylinder" tester [1*b*] using 2 lb. tension and 2 lb. pressure. Number 0 emery paper was employed as the abrasive liner. The results are expressed both as strength retained after selected numbers of abrading cycles and as total number of cycles required for rupture. On this latter basis the polymer coated yarn withstood 319% more cycles than the scoured control.

The frictional properties of the scoured and polymer coated yarns were measured by two different

[3] du Pont acrylic fiber.

procedures and the data reported as a percentage of that obtained with raw cotton. The first method reported involved the measurement of the force required to pull one yarn against another. This force was automatically recorded on a TRI-Schaevitz electronic tester [12]. One length of the test yarn was attached in a vertical position to the movable crosshead and given three twists around another length which was held stationary and at a 10° angle to the first. A tension of 28 g. was applied to the movable yarn and 200 g. tension maintained on the stationary piece. The average differences in registered load when the crosshead was moving downward at 12 in./min. and that registered when the crosshead was moving upward at the same speed were taken as a measure of the frictional forces encountered. The results show the coated yarns to have 30% greater friction than either the raw or scoured yarns. This increased friction is probably a consequence of the roughness of the polymer coating. Another contributing factor may result from the heat of friction, which would tend to bind together the thermoplastic coated yarns.

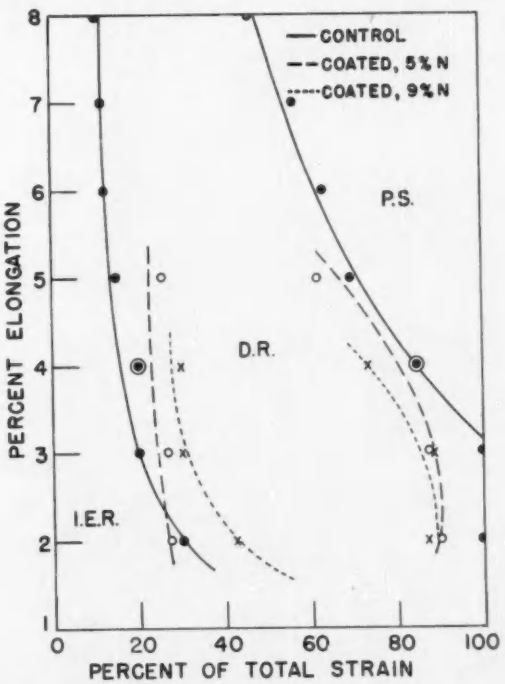


Fig. 3. Elastic properties of polyacrylonitrile coated 14s/2 (42s × 2 tex) scoured cotton yarn.

The other procedure employed was that of Nott and Grant [9] to determine the coefficient of friction, and is a modification of that developed by Buckle and Pollitt [4]. The coefficients were determined from the force required to draw the yarn in a 90° angle over a polished stainless steel cylinder of 1.5-in. diameter. Measurements were recorded only after sufficient preliminary experiments had been conducted with each yarn to result in essentially constant values of the coefficient. Data obtained with this procedure indicated reduced coefficients of friction for both the coated and scoured yarns in comparison with raw yarn.

The elastic properties of a polyacrylonitrile coated yarn and its scoured control are shown in Figure 3. The relaxation and recovery tests were performed by use of the Instron instrument, employing a specimen length of 10 in. and a rate of extension of 1 in./min. The coated specimens exhibited proportionately greater immediate elastic recovery and greater permanent set as the weight of polymer add-on was increased. As a consequence, the delayed elastic recovery was considerably reduced.

The different shapes of the second cycle loading curve, not shown, were of interest. The curve obtained with scoured cotton indicated a gradual load-

TABLE II. Abrasion and Frictional Properties of Polyacrylonitrile Coated 14s/2 (42s × 2 tex) Scoured Cotton Yarn

Test	Scoured control	Coated
Flex abrasion:		
Cycles to rupture	1060	174–178* (164 after softening)
Flat abrasion:		
% Strength retained after		
25 cycles	68.0	89.4
50 cycles	40.5	83.8
100 cycles	failed	75.8
Cycles to rupture	95	398
Frictional properties:		
Force required to pull one yarn against another (% of raw cotton)	99	130
Coefficient of friction determined from force required to draw yarn over a polished ss cylinder (% of raw cotton)	84	84

* Duplicate experiment.

ing, and in the low stress region the modulus passed through a range of values. The coated yarn, however, continued slack to a certain point and then abruptly changed to a virtually constant modulus.

Effect of Degrading Influences

The results of tests for resistance of the coated yarns and their scoured controls to rot, acid, heat, and light degradation are given in Table III. The polyacrylonitrile coating, at a nitrogen level of approximately 5%, offered excellent protection to the yarn against bacteriological attack. This high degree of protection was retained even after application of the softening treatment. The coating also provided improved acid resistance, but did not appreciably alter the behavior of cotton to heat or light degradation.

Results of the outdoor exposure tests and examination of the weathered yarns indicated that the coat-

TABLE III. Resistance of Polyacrylonitrile Coated 14s/2 (42s × 2 tex) Scoured Cotton Yarns to Rot, Acid, Heat, and Light Degradation

(All data reported as percent strength retention relative to that of the original scoured control)

Resistance to rot

Length of time buried, wk.	Scoured control	Coated		Coated and softened	
0	100.0	127.0	136.8*	113.0	114.5*
1	failed	140.1	132.0	115.0	116.3
7	—	137.6	126.2	128.2	124.5
12	—	144.2	—	131.3	—

Resistance to acids

Length of time exposed, min.	Concentrated HCl		45% H_2SO_4	
	Scoured control	Coated	Scoured control	Coated
0	100.0	116.6	100.0	135.6
5	39.8	65.0	86.2	110.7
10	37.9	71.0	72.5	110.8
15	23.0	65.7	62.0	108.4

Resistance to heat

Length of time exposed to 160° C., da.	Scoured control	Coated		Coated, stretched, and tempered	Wet-stretched and coated
0	100.0	122.5	126.0*	128.9	141.0
1	63.4	73.8	75.1	75.0	88.3
2	47.0	49.3	53.3	49.6	58.6
3	41.8	35.5	34.4	45.0	49.8
4	23.5	31.1	29.8	36.2	39.2
7	9.6	13.0	12.8	15.4	19.0

Resistance to light (outdoor exposure)

Length of time exposed, mo.	Scoured control	Wet-stretched and coated		Lead chromate treated	Lead chromate treated and coated
0	100.0	155.0	151.8*	110.2	136.4
1	80.1	141.2	143.9	—	—
2	75.0	128.9	127.6	100.8	115.6
3	63.0	109.1	102.9	88.9	99.1
4	63.3	107.7	99.9	88.5	99.5
5	55.2	84.5	80.3	74.3	83.4
6	43.4	72.0	71.5	64.8	72.7

* Duplicate experiment.

ing was not seriously degraded, although it offered no protection to the cotton core. However, more than 4 mo. of exposure were required to reduce the strength of the wet-stretched and coated yarn to a value equal to that of the unexposed scoured control.

Lead chromate precipitated within the confines of cotton fibers is known to impart a high degree of weather resistance [2]. One of the factors causing a gradual loss in strength of such yarns when exposed to outdoor weathering is presumed to be leaching of the chromate by rain water. The polyacrylonitrile coating was applied to chromate-treated yarns in an attempt to seal in the chromate and reduce leaching. However, the data in Table III shows that no appreciable reduction of the loss in strength of the chromate-treated yarn was achieved by this treatment.

Dyeing Properties

The coated yarns showed similar behavior in their dyeing properties to that exhibited by synthetic acrylic fibers. However, direct cotton dyes could be applied with some degree of success. If the yarns were dyed prior to application of the polymer, deep and bright color shades were clearly discernible through the coating. Only when the quantity of polymer add-on exceeded 15–20% was this color intensity appreciably lessened.

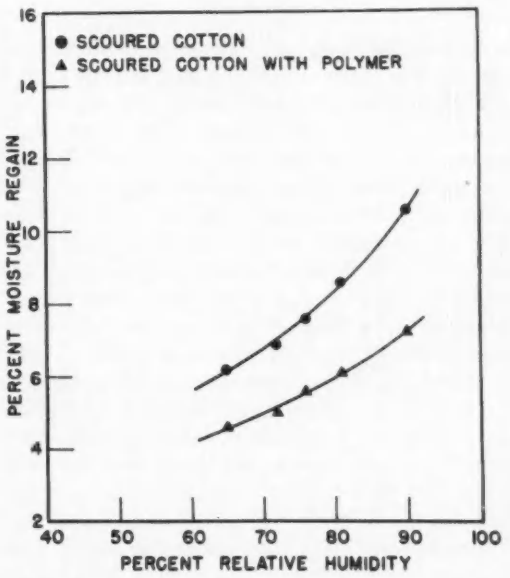


Fig. 4. Effect of atmospheric humidity on moisture regain of polyacrylonitrile coated 14s/2 (42s × 2 tex) cotton yarn.

Moisture Regain

The moisture regain of the scoured cotton yarn, both before and after development of the polymer, was determined by conditioning dry samples to constant weight above salt solutions of known relative humidities. To avoid tendering the cotton cellulose, nitrate salts were not utilized in this study. The data are plotted in Figure 4. The regain of the coated yarn (6.65% nitrogen) is noted to be appreciably less than the uncoated throughout the range of humidities employed. If we assume the regain of the coating to be similar to that reported for Orlon [8], these significant differences in the regain of the two yarn samples cannot be attributed merely to the presence of the polymer. Apparently some bonding between the polyacrylonitrile and the cellulose has occurred to reduce the regain of the cotton fraction. Such bonding could also explain the degree of rot resistance observed.

Density

Measurements of this property upon single fibers extracted from both the polymer coated yarn and its scoured control were made in the density gradient column of Orr and coworkers [10]. A density of 1.404 was determined for coated fibers containing 6.65% nitrogen, as compared with 1.549 for the scoured control. The former value is slightly less than that of 1.422 computed from the addition of the polymer, assuming a value of 1.04 for unoriented polyacrylonitrile [14].

Summary and Conclusions

The polymerization of acrylonitrile vapors within and upon the fiber surfaces of a 14s/2 (42s × 2 tex) scoured cotton yarn has been described. The treated products were found to have materially increased breaking strength, particularly when the polymer was applied to prestretched yarns. Other interesting properties found included excellent resistance to rot, good resistance to flat abrasion and to acid, high frictional characteristics between adjacent yarns, and low density. The coated yarns were, however, low in flex abrasion resistance. This property was not improved by softening the product.

These polyacrylonitrile coated yarns can be prepared with essentially the same equipment and procedures as required for the vapor phase cyanoethylation of cotton; the only exception is that a different catalyst is employed. This illustrates the utility of acrylonitrile for preparation of a variety of useful cotton products.

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Literature Cited

1. Am. Soc. Testing Materials, "ASTM Standards on Textile Materials," (*a*) D1379–55T, (*b*) D1175–55T, Philadelphia (1956).
2. Anonymous, *Agr. Research* **3**, No. 8, 6 (1955).
3. Brownell, C. R., U. S. Patent 2,075,777 (Mar. 30, 1937).
4. Buckle, H. and Pollitt, J., *Shirley Inst. Memoirs* **22**, 1–12 (1948); *J. Textile Inst.* **39**, T199–210 (1948).
5. Gottlieb, I., *Chem. Week* **80**, No. 7, 80 (1957).
6. Gottlieb, I. and Jeffries, E., *Chem. Week* **80**, No. 11, 112–114, 116 (1957).
7. Madaras, G. W. and Speakman, J. B., *J. Soc. Dyers Colourists* **70**, 112–116 (1954).
8. Mauersberger, H. R., *American Handbook of Synthetic Textiles*, Textile Book Publishers, Inc., New York (1952).
9. Nott, E. H. and Grant, J. N., TEXTILE RESEARCH JOURNAL **26**, 673–680 (1956).
10. Orr, R. S., Weiss, L. C., Moore, H. B., and Grant, J. N., TEXTILE RESEARCH JOURNAL **25**, 592–600 (1955).
11. Philipp, H. J. and Conrad, C. M., *J. Appl. Phys.* **16**, 32–40 (1945).
12. Reichardt, C. H., Schaevitz, H., and Dillon, J. H., *Rev. Sci. Instr.* **20**, 509–516 (1949).
13. Valentine, L., *J. Textile Inst.* **46**, T270–283 (1955).
14. Valentine, L., *J. Textile Inst.* **47**, T1–15 (1956).

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The Effect of Construction on Certain Stress-Strain Properties of Uncoated and Coated Fortisan Fabrics[1]

J. F. Krasny and A. M. Sookne

Harris Research Laboratories, Inc., Washington, D. C.

G. D. Mallory and J. K. Phillips

Goodyear Tire and Rubber Company, Akron, Ohio

Abstract

The stress–strain properties of 135 systematically varied Fortisan filament fabrics were investigated before and after coating with rubber and after controlled flexing of the coated fabrics. In the uncoated fabrics, the highest tenacity was attained in a wide range of fabrics which were neither too dense nor too sleazy and which had few yarns of relatively high denier rather than many low denier yarns per inch. The structural tenacity (breaking load of the coated fabrics in the warp or filling direction divided by the weight of the uncoated warp or filling) of the coated fabrics followed roughly the same pattern, but was more sensitive to sleaziness. The range of coated fabrics which retained comparatively high structural tenacity after flexing was limited to those woven with the lowest denier yarns with a combination of a high number of yarns per inch and a rather open weave (2/2, 4/2, 5/1, or 4/4 twill) or a lower number of yarns per inch and a denser weave, such as 2/1 twill or 4 shaft sateen.

Introduction

Cotton is perhaps the most commonly employed fiber in rubber coated fabrics. The strength per unit weight of such fabrics can be substantially improved by use of a stronger fiber in filament form; however, some of the stronger yarn types present difficulties of coating adhesion and continued growth under strain, while others extend so little that a low flex resistance of the coated fabrics may result. The present work represents an attempt to determine experimentally the optimum weave, yarn denier, number of plies, and twist for such a low extension yarn, Fortisan, to obtain the best combination of strength and resistance to damage by flexing of rubber coated fabrics made from it.

The effect of fabric construction on fabric properties has been the subject of many studies. An excellent survey of those prior to 1952 can be found in Part B of Kaswell's *Textile Fibers, Yarns, and Fabrics* [2]. Recent papers in this field include those of Jameson, Whittier, and Schiefer [1] on rayon fabrics, and Woo and Montgomery's study [4] of the effect of construction and fiber type on two-dimensional stress–strain properties of fabrics.

The present work is concerned with the strength and ultimate elongation of a variety of experimental Fortisan fabrics and with the strength and flex resistance of the same fabrics after coating with rubber. Wide variations in weave, yarn denier, and twist were included in the fabrics studied. The crease recovery of the uncoated fabrics has been discussed in a previous paper [3].

Materials and Methods

Each of the eleven fabric series (five weighing approximately 2 oz./sq. yd. and six weighing 3 oz./sq. yd) consisted of ten or eleven individual fabrics woven with the same number of yarns per inch and yarn type in both warp and filling but differing in weave (Table I). The fabrics varied from very tight (close yarn spacing, short float weaves) to very open (high denier yarns spaced widely, long

[1] Contribution No. 216 from the Goodyear Tire and Rubber Company Research Laboratory.

TABLE I. Construction Specifications of "Balanced Series"

Series*	Single yarn,† den./fil.	Single twist,† t.p.i.	Number of plies†	Ply twist,† t.p.i.	Yarns/in.†	Fabric wt., oz./sq. yd.	Cover factor†
1	30/40	2.5S	2	4.8S	116	1.8	12.4
2	30/40	2.5S	2	4.8S	167	2.6	17.7
3	90/120	7.1S	1		80	1.9	10.4
4	90/120	7.1S	1		118	2.8	15.3
5	60/80	2.5S	2	2.7S	60	1.8	8.9
6	60/80	2.5S	2	2.7S	90	2.9	13.4
7	60/80	2.5S	3	2.1S	40	1.8	7.4
8	60/80	2.5S	3	2.1S	60	2.8	11.1
9	90/120	2.5S	2	2.5S	40	1.9	7.4
10	90/120	2.5S	2	2.5S	60	2.9	11.1
11	90/120	2.5S	4	1.9S	32	2.9	8.2

* Each series contains eleven or twelve fabrics differing in weave.
† The same in warp and filling.

TABLE II. Tenacity* of Uncoated Fabrics, g./den.

	Plain weave		2/1 Twill		2/2 Twill 2 x 2 Basket 4 Shaft sateen		5/1 Twill 4/2 Twill		4/4 Twill 8 Shaft sateen		11/1 Twill 10/2 Twill		Series average	
Series	W	F	W	F	W	F	W	F	W	F	W	F	W	F
1	4.86	5.64	5.40	6.16	6.00	6.28	5.54	6.02	6.26	6.34	6.22	6.04	5.90	6.14
2	—	—	3.68	5.88	5.40	5.84	5.84	6.18	6.10	6.06	5.94	5.80	5.58	5.86
3	5.76	5.32	5.46	5.96	6.04	6.26	5.68	5.90	5.80	6.32	5.90	6.62	5.84	6.24
4	—	—	5.28	5.86	5.86	6.04	5.92	6.46	6.04	6.70	6.14	6.36	5.90	6.30
5	5.64	6.20	5.84	6.18	6.00	6.36	6.14	6.10	6.02	6.16	5.98	6.02	6.00	6.14
6	—	—	4.94	5.72	4.88	5.70	5.40	5.80	5.22	6.12	6.22	5.56	5.32	5.76
7	6.14	6.42	6.66	6.48	6.58	6.72	6.68	6.72	6.76	6.80	6.42	6.08	6.62	6.56
8	5.72	6.46	5.84	6.62	6.46	6.58	6.50	6.82	6.54	6.74	6.42	6.80	6.40	6.74
9	5.98	6.10	6.18	6.16	6.22	7.00	6.32	6.14	6.08	6.52	6.10	5.94	6.18	6.44
10	—	—	6.30	5.88	6.06	6.30	6.00	6.20	6.00	6.32	6.08	6.08	6.06	6.16
11	6.04	6.68	6.96	7.22	6.38	6.76	6.36	5.74	6.28	6.62	6.44	6.02	6.44	6.62

* Tenacity: Breaking load of the warp or filling direction divided by the warp or filling weight.

TABLE III. Structural Tenacity* of Coated Fabrics, g./den.

	Plain weave		2/1 Twill		2/2 Twill 2 x 2 Basket 4 Shaft sateen		5/1 Twill 4/2 Twill		4/4 Twill 8 Shaft sateen		11/1 Twill 10/2 Twill		Series average	
Series	W	F	W	F	W	F	W	F	W	F	W	F	W	F
1	—	—	6.72	6.90	6.16	6.14	6.02	5.78	6.24	5.72	5.50	6.12	6.06	5.88
2	—	—	4.28	6.18	5.48	6.20	6.72	6.46	6.12	6.48	4.94	5.66	5.64	6.22
3	6.34	5.66	6.78	7.44	6.94	6.96	6.74	6.26	6.96	6.22	6.86	4.94	6.68	6.36
4	—	—	6.06	5.86	6.24	5.62	6.50	6.42	6.52	6.50	5.88	5.88	6.18	5.92
5	6.40	6.76	6.12	5.28	6.58	6.28	6.22	5.46	5.80	4.92	6.14	4.56	6.12	5.44
6	—	—	5.34	4.80	6.02	3.84	6.22	4.68	5.84	3.96	6.92	3.84	6.14	4.08
7	6.72	6.74	6.64	5.76	6.84	5.94	6.94	5.02	6.98	4.56	6.98	4.34	6.90	5.10
8	6.76	7.06	7.28	6.82	6.62	6.68	6.44	6.34	6.66	6.12	7.20	5.46	6.80	6.28
9	6.70	6.02	6.46	6.56	6.90	5.48	6.78	4.76	6.46	4.54	5.98	4.66	6.48	4.84
10	6.34	6.32	7.02	7.04	6.78	6.72	6.16	6.58	6.80	6.12	6.16	5.98	6.52	6.36
11	6.66	6.24	6.78	5.78	6.62	5.84	6.34	5.86	6.20	4.92	5.66	3.72	6.30	5.32

* Structural tenacity: Breaking load of the coated fabric in the warp or filling direction divided by the weight of the uncoated warp or filling.

float weaves). The weaves are shown in the column headings of Table VI.

All fabrics were prepared and desized at the Philadelphia Textile Institute. Part of each fabric was coated with a rubber compound by the Research Division of the Goodyear Tire and Rubber Company. The coating thickness was about 1 mil, and the coating weight was about 1.25 oz./sq. yd. on each side of the fabric. The coating method allowed very little penetration of the coating compound into the fabrics except those with large interstices.

The coated fabrics were die cut into strips $\frac{3}{4}$ in. wide and 7 in. long. One set of such specimens was tested for tensile properties before flexing, and another was subjected to 300 flex cycles on an M.I.T. folding endurance tester and then broken on a Scott pendulum-type tester. Specimens of the uncoated fabrics raveled to a width of $\frac{3}{4}$ in. were broken on a Tinius Olsen Electromatic Testing Machine. This is an instrument which is essentially free from inertia effects and which permits the precise measurement of small elongations. The uncoated fabrics were tested at 70° F. and 65% relative humidity, the coated fabrics at 75° F. and 55% relative humidity.

Results and Discussion

In a previous paper discussing the crease recovery of the same fabrics [3], the tightness [2] was chosen as the independent variable in graphical representation of the results. While the tightness is still important in the present discussion of the fabric strength, rather complicated interactions between the independent variables (yarns per inch, single yarn denier, number of plies, weave) preclude simple graphical representation of the data; they must be analyzed by means of tables. In Tables II–V, a concession has been made to convenience by giving average figures for fabrics of any of the individual series having the same number of yarns per weave repeat (e.g., 2/2 twill, 2 × 2 basket, and 4 shaft sateen have a weave repeat of 4; i.e., the same type interlacing of warp and filling occurs every four yarns). This averaging procedure is deemed defensible because the individual fabrics so grouped generally did not differ significantly in properties. The 12 × 12 basket weave fabrics with twill line were not included in any of the groups; their strength, especially when coated, was often low, possibly because the complicated weave causes poor stress distribution among the yarns.

Two and three ounce fabrics incorporating one yarn type are listed in neighboring rows in Tables II–V for ease of comparison. The pairs are arranged in ascending order of total yarn denier. In the last two columns, the average value for each series of fabrics is given. In some cases, these averages are not representative of the behavior of the particular series because of the interaction of weave and fabric construction. However, by comparing the individual values with the series averages, the analysis of the

[2] Tightness is defined as the number of weave repeats per inch. This is large when there are many yarns per inch and the weaves have short floats; i.e., the yarns of one system (warp or filling) cross over only 1–3 yarns of the other system between points of interlacing.

TABLE IV. Structural Tenacity* of Coated Fabrics After Flexing, g./den.

	Plain weave		2/1 Twill		2/2 Twill 2 x 2 Basket 4 Shaft sateen		5/1 Twill 4/2 Twill		4/4 Twill 8 Shaft sateen		11/1 Twill 10/2 Twill		Series average		Series average % strength retained after flexing	
Series	W	F	W	F	W	F	W	F	W	F	W	F	W	F	W	F
1	—	—	5.78	5.60	5.82	5.46	5.52	4.96	5.62	5.24	5.48	5.38	5.60	5.24	92	89
2	—	—	4.20	5.32	5.32	5.52	5.84	6.14	5.74	5.82	4.92	5.36	5.32	5.62	94	90
3	5.38	5.14	5.22	5.30	5.10	5.48	4.96	5.60	4.76	4.90	4.82	4.54	4.92	5.10	74	80
4	—	—	5.36	4.90	5.12	5.04	5.10	5.62	5.20	5.32	5.00	5.52	5.08	5.20	82	88
5	5.18	5.12	5.08	4.86	5.20	5.12	4.86	4.70	4.68	4.58	4.94	3.90	4.90	4.65	80	86
6	—	—	3.58	4.78	3.76	3.72	3.96	4.74	3.70	3.72	4.26	3.68	3.88	3.98	63	98
7	5.00	4.44	4.70	4.34	4.70	4.36	4.66	3.92	4.60	3.82	4.54	2.88	4.64	3.82	67	75
8	4.92	4.60	5.02	5.00	4.70	4.44	4.78	4.66	4.88	4.00	4.48	4.04	4.78	4.38	70	79
9	4.86	4.60	4.52	4.30	4.66	4.46	4.64	4.04	4.50	3.36	4.36	4.12	4.54	4.04	70	84
10	5.12	4.78	5.24	5.04	4.72	4.84	4.78	4.48	4.66	4.50	4.62	4.22	4.72	4.52	72	71
11	5.20	5.22	5.00	4.60	5.12	4.80	4.96	4.64	4.92	4.00	4.58	3.16	4.90	4.28	78	80

* Structural tenacity: Breaking load of the coated fabric in the warp or filling direction divided by the weight of the uncoated warp or filling.

TABLE V. Elongation at Break of Uncoated Fabrics, %

Series	Plain weave		2/1 Twill		2/2 Twill 2 x 2 Basket 4 Shaft sateen		5/1 Twill 4/2 Twill		4/4 Twill 8 Shaft sateen		11/1 Twill 10/2 Twill		Series average	
	W	F	W	F	W	F	W	F	W	F	W	F	W	F
1	11.8	8.2	9.0	8.5	8.4	8.5	8.1	8.4	8.2	8.6	8.3	8.1	8.3	8.4
2	—	—	17.0	11.3	13.2	11.6	11.8	11.5	10.1	10.3	9.4	10.4	12.0	11.1
3	9.2	8.9	7.8	8.6	8.1	8.4	7.7	7.9	8.0	8.0	7.6	9.6	7.9	8.3
4	—	—	15.0	10.8	11.2	10.4	10.5	10.3	8.9	10.1	9.1	10.1	10.6	10.4
5	8.2	8.2	7.8	8.3	7.9	8.1	7.4	7.9	7.8	7.9	7.6	8.2	7.7	8.0
6	—	—	7.2	12.2	6.9	11.7	6.7	12.5	7.3	10.7	7.4	11.3	7.0	11.7
7	7.9	8.5	7.7	8.0	8.2	8.4	8.1	8.6	8.3	8.8	8.3	8.3	8.1	8.4
8	10.3	10.2	8.9	9.4	8.9	9.4	9.1	9.5	9.4	9.1	9.1	9.4	9.1	9.4
9	7.9	8.2	7.8	7.5	7.7	8.3	7.7	7.9	7.6	8.7	7.6	7.5	7.6	8.1
10	—	—	9.5	8.9	8.5	8.9	8.3	8.7	8.1	9.0	8.3	8.7	8.4	8.8
11	8.7	9.4	9.8	9.7	8.3	9.5	8.5	9.4	8.4	8.9	8.3	9.0	8.5	9.3

TABLE VI. Tenacity, Structural Tenacity, Strength Loss, and Elongation at Break Averaged for Fabrics Woven in One Weave

	Twill							Basket		Sateen	
Tenacity of uncoated fabrics**	2/1	5/1	11/1	2/2	4/2	10/2	4/4	2 x 2	12 x 12*	4 Shaft	8 Shaft
Average, all series, warp, g./den.	5.68	6.08	6.06	5.98	6.00	6.28	6.10	6.06	6.02	5.94	6.10
Average, all series, filling, g./den.	6.20	6.60	6.16	6.46	6.26	6.10	6.50	6.34	6.20	6.26	6.34
Average, Series 1, 2, 3, 4, warp, g./den.	4.96	5.68	5.94	5.80	5.80	6.14	6.14	5.96	5.80	5.72	5.96
Average, Series 1, 2, 3, 4, filling, g./den.	5.96	6.28	6.42	6.16	6.00	6.04	6.52	6.12	6.08	6.04	6.18
Structural tenacity† of coated fabrics											
Average, all series, warp, g./den.	6.32	6.38	6.30	6.42	6.52	6.10	6.62	6.48	5.96	6.50	6.22
Average, all series, filling, g./den.	6.04	5.54	4.96	5.92	5.84	5.06	5.56	5.92	5.46	6.04	5.76
Average, Series 1, 2, 3, 4, warp, g./den.	5.96	6.40	5.94	6.22	6.58	5.76	6.60	6.04	5.52	6.36	6.30
Average, Series 1, 2, 3, 4, filling, g./den.	6.60	5.76	5.56	6.38	6.30	5.74	6.16	6.22	6.00	6.08	6.30
Structural tenacity of coated† fabrics after flexing											
Average, all series, warp, g./den.	4.88	4.90	4.72	4.98	4.94	4.70	4.90	4.82	4.66	4.98	4.78
Average, all series, filling, g./den.	4.92	4.80	4.24	5.00	4.92	4.28	4.54	4.66	4.24	4.86	4.40
Average, Series 1, 2, 3, 4, warp, g./den.	5.14	5.44	5.12	5.64	5.32	5.00	5.46	5.00	4.76	5.40	5.20
Average, Series 1, 2, 3, 4, filling, g./den.	5.28	5.32	5.16	5.74	5.84	5.24	5.20	5.00	4.64	5.38	5.44
% Strength retained after flexing											
Average, all series, warp	77	77	75	78	76	77	76	74	78	77	77
Average, all series, filling	82	87	86	84	84	85	82	79	78	80	82
Average, Series 1, 2, 3, 4, warp	86	85	88	91	79	87	83	83	86	85	83
Average, Series 1, 2, 3, 4, filling	80	92	93	90	93	91	84	80	77	89	86
Elongation at break of uncoated fabric, %											
Average, all series, warp	9.8	8.6	8.3	9.0	8.4	8.2	8.4	8.6	8.7	9.0	8.3
Average, all series, filling	9.4	9.5	9.2	9.6	9.2	8.9	9.0	9.2	9.4	9.4	9.1
Average, Series 1, 2, 3, 4	12.2	9.9	8.6	10.4	9.1	8.5	8.9	9.8	9.9	10.5	8.7
Average, Series 1, 2, 3, 4	9.8	9.7	9.7	9.8	9.3	8.9	9.4	9.6	9.9	9.8	9.1

* With twill line.

** Tenacity: Breaking load in the warp or filling direction divided by warp or filling weight.

† Structural tenacity: Breaking load of the coated fabric in the warp or filling direction divided by the weight of the uncoated warp or filling.

interactions of weave, denier, and number of yarns per inch may be facilitated.

Table VI shows the averages obtained when (a) the values obtained for the fabrics for all series, woven in one weave, were averaged, and (b) the corresponding values were averaged for only the rather tight Series 1, 2, 3, and 4. In the latter averages, certain patterns appeared more clearly than in the general averages, because the individual values showed less variability than those of the open sleazy fabrics of the other series.

Presented below is a qualitative analysis of certain trends, some applicable to all fabrics, others only to those of rather tight construction.

Tenacity of the Uncoated Fabrics

Tenacity here expressed the breaking load (in grams) divided by the denier of the stressed yarn system (warp or filling). The following trends can be detected:

1. The fabric tenacity is generally low in extremely tight and in extremely open fabrics. In the tight fabrics; i.e., those woven with short float weaves such as plain weave, 2/1 twill, and 4 shaft sateen from the series with high cover factor, the angle formed by the filaments with the direction of strain may account for the low strength. Since the effect of fabric tightness on strength is more apparent in the warp than in the filling direction, it also seems that the warp of the tight fabric suffered some damage in weaving.

The low strength of some of the very open fabrics; i.e., those with low cover factor and/or long float weaves, may be due to the shifting of the yarns and their resulting waviness in the fabric plane, which could cause uneven distribution of the stress among the yarns during the breaking test.

2. The 2-oz. fabrics usually had higher tenacities than the 3-oz. fabrics woven in the same weave from the same yarn type. This effect was more apparent in the warp than in the filling, in the short float than the open weaves, and in the ply-yarn series than in the series woven with 90/1 yarns (Series 3 and 4).

3. In fabrics comparable in weight and weave, the tenacity increased with increasing total yarn denier and correspondingly wider spacing. There was, however, little difference in this respect among the fabrics of the lighter weight (2-oz.) group woven with 60/2, 90/1, and 30/2 yarns. The effect of yarn denier, like most other effects, was less clearly discernible in open weave fabrics.

4. The fabrics woven with 60/3 (Series 7 and 8) were generally stronger than comparable fabrics from 90/2 yarns (Series 9 and 10).

5. The weave had an effect on the tenacity mostly insofar as the number of yarns per repeat and thus the tightness was concerned (see also Table VI). No consistent effect of the kind of weave, such as twill, basket, or sateen, could be detected; however, the tenacity often increased as the number of yarns per repeat increased, and the increase was larger between the 2/1 twill and the group comprising 2/2 twill, 2/2 basket, and 4 shaft sateen than between the 4/4 twill-8 shaft sateen and the 11/1–10/2 twill group. The 2/1 twill seemed generally to be below the 2/2, and the 4/2 was below the 4/4 twill in tenacity. The 12×12 basket was woven with a twill line, and was low in tenacity, probably because of the above-mentioned unfavorable stress distribution.

6. The fabrics of Series 6 frequently behaved differently from the general trends described before, perhaps because their warp had inadvertently been strained more in weaving. This series had low warp crimp (average 0.6%) and high filling crimp (average 6.1%), while in all other series warp and filling crimp were almost equal (averaging 2.1 and 2.2% respectively). The tenacity of Series 6 was quite low in both warp and filling.

7. The filling strength generally exceeded that of the warp, and this difference was larger in tight fabrics. This may be due, as mentioned before, to overstraining of the warp during wearing.

Structural Tenacity—Coated Fabrics

There are several means of expressing the strength of the coated fabrics, all of which have certain advantages and disadvantages for the present purpose. If one expresses the strength in pounds per unit width, the comparison of fabrics of different weight is made difficult. For many purposes, the strength in pounds or grams per unit of the weight of the coated fabric would be most advantageous. However, the object of the present study was to find, by variations in the construction, the most effective fabric structure; i.e., the most favorable ratio of coated fabric strength to uncoated fabric weight. Thus, the units chosen to represent the data were the warp or filling breaking load of the coated fabrics.

expressed in grams, divided by the weight of the uncoated warp or filling yarns, expressed in denier. This will be called structural tenacity throughout this paper.

The effect of elastic coatings on the strength of the coated as compared to that of the uncoated fabrics may be assumed to be twofold. First, the coating may contribute to the fabric strength by its own resistance to extension; this contribution is small when, as in the present case, the fabric is rather inextensible and the coating relatively extensible.

The second effect of the coating is the restraint of the movement of the yarns to achieve a better stress distribution under tension, and thus a lowering of the structural tenacity; i.e., the efficiency of the fabric as a load-bearing member of the coated fabric assembly. Obviously, this latter factor will be affected not only by the relative extensibility of the fabric and coating but also the depth of penetration of the coating into the fabric. Time did not permit a detailed study of the penetration of the coating into the various fabrics.

The trends in structural tenacity as defined here parallel, of course, those in absolute strength with respect to the effect of weave, denier, and numbers of yarns within each fabric weight group. The absolute strength of the 3-oz. series was higher than the 2-oz. fabrics, though the latter often had higher structural tenacity. Similarly, the structural tenacity trends would frequently not parallel the trends observed if the fabric strengths were expressed in strength per unit weight of coated fabric. In the latter system, the differences between fabrics would appear smaller, and, in the case of 2- and 3-oz. fabrics, sometimes reversed as compared to the structural tenacity shown in the tables.

The following trends seem to emerge from an analysis of the data of Table III:

1. The combination of short float weave and very close yarn spacing (Series 2 and 4) produced low structural tenacities, especially in the warp direction. Except in these cases of extreme tightness, a downward trend of structural tenacity with increasing openness of the weave could be detected, especially in the filling direction.

2. The structural tenacities of the 2- and 3-oz. fabrics woven with the same yarns compared as follows: in the case of the 60/3 (Series 7 and 8) and 90/2 (Series 9 and 10) yarns, the filling structural tenacities of the 2-oz. fabrics were usually lower. However, in the case of the denser fabrics woven with finer yarns (Series 1, 2, 3, and 4), the structural tenacities of the 3-oz. fabrics were often lower. There were numerous exceptions, especially in the more open weaves.

3. The warp structural tenacities of fabrics comparable in weight and weave generally increased with increasing yarn denier, except that the firm 90/1 fabrics (Series 3 and 4) ranked comparatively high, and the sleazy 90/4 (Series 11) low. The filling structural tenacities showed no clear effect of the denier.

4. The 60/3 (Series 7 and 8) fabrics again may have been somewhat superior to the comparable 90/2 fabrics (Series 9 and 10).

5. The weave was, as it had been among the uncoated fabrics, of lesser importance than yarn spacing. However, a downward trend with increasing openness of the weave was evident, especially in the filling, and in the heavier fabric group (see also Table VI). In the warp, the maximum structural tenacities were often obtained in the weaves with an intermediate (6–8) number of yarns per repeat. The 12 × 12 basket weave with a twill line again ranked rather low.

6. Series 6 often behaved differently from the other series, as it had in the case of the uncoated fabrics. In the warp direction where there was low crimp, coating strengthened the fabrics considerably. In the filling, which had comparatively high crimp, strength was greatly reduced by coating.

7. In contrast with the uncoated fabrics, the warp strength generally exceeded that of the filling in all but the most closely spaced Series 2. The difference often increased with increasing length of the weave float. This finding can probably be explained by the observation that the filling yarns in general, and both warp and filling yarns in the open fabrics, appeared to have a relatively low degree of parallel alignment.

Structural Tenacities of Coated Fabrics after Flexing

Table IV shows the following trends with respect to the interaction of fabric construction parameters and strength retained by the coated fabrics after flexing:

1. In order to obtain optimum structural tenacities after flexing, too tight or too open fabric structure must be avoided. Thus, in Series 2, which contained many yarns per inch, the optimum values were ob-

tained with medium float weaves such as 5/1, 4/2, and 4/4 twill; in Series 8 and 10, with an intermediate cover factor, the short float 2/1 twill gave the highest strength; in the open Series 7, 9, and 11, the plain weave was best. The structural tenacities generally fell off rapidly with increasing length of float, especially in the filling.

2. A comparison of the 2- and 3-oz. series woven with one yarn type showed that in tight fabrics the 2-oz. fabrics were higher in structural tenacity after flexing, but when the fabric openness was increased by wider yarn spacing and/or longer float weaves, the 3-oz. fabrics were better. Thus, the 2/1 twill and 4 shaft sateen of Series 1 (2 oz.) had higher structural tenacities than their counterparts of Series 2 (3 oz.); in the more open constructions; e.g., Series 7, 8, 9, and 10, the 3-oz. fabrics lead in structural tenacity after flexing, especially in the filling.

3. The structural tenacities of the flexed coated fabrics were reduced by increasing yarn denier; the two 30/2 series and 60/2 generally were considerably better than those with heavier denier.

4. Series 6 generally exhibited rather low structural tenacities after coating in both the warp and filling direction. However, on a basis of percent of original strength retained after flexing (shown in the last columns of Table IV) its low crimp warp rated lowest, and the high crimp filling highest among all series averages. It thus seems that high crimp, which caused low original coated fabric strength due to unfavorable angles between the yarn axis and the stress, was advantageous from a flex resistance point of view.

5. The warp strength after coating and flexing exceeded that in the filling in the open fabrics; i.e., those with long float weaves and/or wide yarn spacing.

6. The 2/2 twill generally rated higher than the 2 × 2 basket weave, especially in the closely spaced Series 1, 2, 3, and 4.

7. The last two columns of Table IV show that, percentagewise, the highest strength retention found was in Series 1 and 2, woven from the lowest denier yarns. The high crimp filling of Series 6 also showed good strength retention, as stated above. The effect of the weave, yarn denier, warp and filling, and fabric weight on the strength retention was indistinct.

Elongation at Break of Uncoated Fabrics

The data in Table V show the following trends:

1. The elongation at break decreased with increasing float length, especially in the warp; in the series with a cover factor below 10, this effect was much less marked. The combination of short float weave and close yarn spacing, which produced low strength, also produced relatively high crimp and high elongation values.

2. For the same weave and yarn denier, the elongation (and crimp) increased with increasing number of yarns per inch, particularly in short float weaves and in the warp.

3. The choice of yarn denier did not seem to affect the elongation to a marked extent.

4. Warp and filling elongations were about equal in all series except Series 6, in which the warp elongation was low, the filling elongation high; this corresponds to the crimp relationships in this series.

Conclusions

The conclusions are a presentation of the most salient findings from a different point of view.

To obtain high uncoated fabric tenacity, neither too dense nor too sleazy constructions should be used. If a coarse yarn denier and low number of yarns per inch are chosen, the weave should have short floats, while for closely spaced fine yarns an opener weave appeared to give more favorable results. The fabric strength apparently depended mainly on the angle of the yarns with the direction of tension, which was high in tight fabrics due to the crimp, and on the stress distribution among the yarns, which may be uneven in sleazy fabrics due to yarn shift and resulting waviness. The warp yarns of Fortisan also seemed to suffer mechanical damage in weaving of tight fabrics. The highest tenacities were found in fabrics woven with 60/3 yarn.

Coating with rubber compounds restricted the yarns in their movement to some extent; both the angle between the yarns and the tension, whether due to crimp or waviness of the yarns, apparently could not be as readily reduced by rearrangement of the yarns under stress as in uncoated fabrics. Thus the warp, which was generally more favorably oriented, gained in structural tenacity by coating while the filling lost. The short float weaves and the 4/4 twill of Series 8 (3-oz. fabric woven with

60/3 yarn) and of Series 3 (2-oz. fabric woven with 90/1 yarn) seemed to give the highest structural tenacities.

The strength of the flexed coated fabrics was enhanced by high original fabric strength, and perhaps by relatively low thickness and low degree of penetration of the coating compound. This point was studied only qualitatively. Thus, as the yarn denier was increased in each weight group (Series 1–5, 2 oz. and 6–11, 3 oz.) the thickness increased; due to the larger spaces between yarns, presumably so did the penetration. The flexed structural tenacities decreased. However, with the denier constant, when the number of yarns and thus the weight was increased, the thickness was also increased somewhat; this apparently was outweighed by less penetration because the structural tenacity generally increased. With increasing float length, thickness and possibly penetration increased, and the structural tenacity decreased. High crimp may also enhance flex resistance, as shown by Series 6. The most favorable structural tenacities after coating and flexing were found in the fabrics woven in intermediate float weaves from the densely spaced low denier yarns of Series 2.

Acknowledgment

Thanks are due to the Goodyear Tire and Rubber Company for permission to publish this work.

Literature Cited

1. Jameson, L. H., Whittier, B. L., and Schiefer, H. F., "Factors Affecting Properties of Rayon Fabrics," TEXTILE RESEARCH JOURNAL **22**, 599 (1952).
2. Kaswell, E. R., *Textile Fibers, Yarns, and Fabrics*, Reinhold Publishing Corporation, New York (1955).
3. Krasny, J. F., Mallory, G. D., Phillips, J. K., and Sookne, A. M., "Crease Recovery of Fabrics. II. Effect of Construction on Crease Recovery of Fortisan Fabrics," TEXTILE RESEARCH JOURNAL **25**, 498 (1955).
4. Woo, H. K. and Montgomery, D. J., "Effects of Construction and Fiber Type on Two-Dimensional Stress-Strain Properties of Fabrics," TEXTILE RESEARCH JOURNAL **23**, 925 (1953).

Manuscript received July 15, 1957.

Letters to the Editor

Short communications in the form of Letters to the Editor are intended to provide prompt publication of significant new research results and to permit an exchange of views on papers previously published in the JOURNAL. These communications are not submitted to formal review as are research papers, and the editors do not assume any share of the author's responsibility for the information given or the opinions expressed. When work previously published in the JOURNAL is the subject of critical comment, the authors of the original paper are given an opportunity to submit a reply, which will be published concurrently when possible.

Cotton Fiber Maturity Rapidly Predicted with Variable Volume of Sample in Micronaire

Southwestern Cotton Ginning Research Laboratory
Agricultural Research Service
U. S. Department of Agriculture
P. O. Box 578
Mesilla Park, New Mexico
and
Agronomy Department
New Mexico Experiment Station
State College, New Mexico
August 1, 1957

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

This communication is submitted jointly by us because it may afford material assistance for cotton breeders and fiber technologists to learn of our new and quick method for predicting fiber maturity, which has thus far given accurate results. For the first time we are making a full disclosure of our apparatus and method, trusting that it may be of wide service to our fellow workers.

To expedite cooperative studies, Mr. Glen Staten suggested that the Fiber Clinic of the U.S.D.A. Cotton Ginning Research Laboratory might develop a quicker and equally accurate method of predicting fiber maturity than had heretofore been used.

On June 11, 1957, preliminary experimental tests were begun with the Micronaire cotton fiber fineness testing instrument to explore its possibilities for making rapid determinations of cotton fiber maturity.

The principle employed in these studies was that of increasing the cubic volume of the standard 50-grain samples over that employed in the regular Micronaire tests. With the 1-in. inside diameter cylinder, the experimental increase was 0.3927 cu. in. for a ½-in. lift of the plunger. This ½-in. increase in vertical dimension of the volume afforded a highly satisfactory range in the curvilinear scale for upland cottons, because greater distention of volumes did not work within the limits of said scale.

Figure 1 depicts the Micronaire instrument and ½-in. spacer employed by the writers.

A total of 57 samples of irrigated Southwestern cottons were used in these experiments, representing harvests before and after frost; the varieties included Acala 1517C, Acala 44WR, Lankart 57, Mesilla Valley, and unknown varieties obtained from bales stored at the local compress, as well as badly damaged samples from a pink bollworm research project at College Station, Texas.

The experimental testing procedure with the ½-in. spacer was as follows:

1. Use standard atmospheric conditions of 65% RH and 70° F.
2. Use standard Micronaire air pressure.
3. After inserting sample into chamber, place ½-in. spacer between plunger and top of chamber wall (Figure 1).

Fig. 1. Photograph shows Micronaire with ½-in. spacer used to increase volume of fiber specimen; difference between Micronaire readings with and without spacer predicts cotton fiber maturity.

4. While holding plunger against ½-in. spacer, release air with pedal and record reading on Micronaire scale.

5. Remove spacer, let specimen remain in chamber, insert and fix plunger at full depth, and make usual Micronaire reading for fineness.

6. Subtract the usual Micronaire reading from the reading made with the spacer.

7. The difference between the two readings can be substituted for x in the formula in Figure 2 to predict fiber maturity.

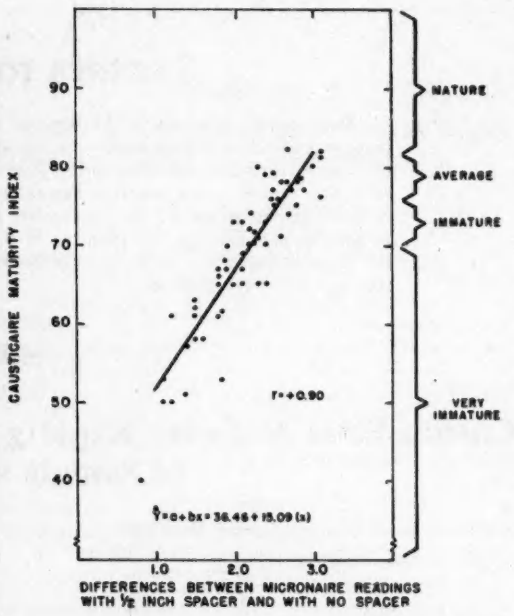

Fig. 2. Relationships between Causticaire maturity indexes and differences between Micronaire upland curvilinear scale readings with and without ½-in. spacer.

Both fineness and maturity values are obtained very rapidly with the same specimen of fibers.

The 57 samples ranged in Causticaire maturity index from 40 to 82. When these were plotted against conventional Micronaire units, which ranged from 2.4 to 5.0, the regression line was curvilinear. However, when the differences between the readings with ½-in. spacer and no spacer were plotted against Causticaire maturity, a straight regression line was produced, as shown in Figure 2. The correlation coefficient was found to be + 0.90.

WALTER E. CHAPMAN, JR.
Cotton Technologist

GLEN STATEN
Agronomist

Quantitative Determination of Cyclohexylamine in Rayon Spin Baths

Research Laboratory
Mo & Domsjö AB
Örnsköldsvik, Sweden
July 26, 1957

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

Cyclohexylamine may sometimes be used as an additive in rayon spin baths [2] in production of high tenacity yarns. During the spinning process, some amine is carried away by the fibers; in order to maintain the amine in the correct concentration range, it is necessary to determine its concentration. This may be done by extracting an alkaline portion of the spin bath with an organic solvent; this method, however, is not very accurate, as the concentration is rather low (1 g./l. or less) and other organic additives may interfere.

Cyclohexylamine has been reported to form an azeotropic mixture with water [1] which boils at 94–95° C. (748 mm. Hg) and contains 59% amine. Thus, it should be possible to collect the amine quantitatively in a small volume of water by distillation of a portion of the spin bath which has been made alkaline. A series of experiments along this line resulted in a simple and accurate procedure for the determination of cyclohexylamine.

Eighty milliliters of an aqueous solution of cyclohexylamine was distilled and the amine content in different fractions determined by titration with 0.1 *N* HCl soln. As seen in Table I, the amine is recovered in the first 15% of distillate.

TABLE I. Recovery of Cyclohexylamine by Distillation of its Aqueous Solution

Fraction	Volume, ml.	Recovered amine	
		mmol.	%
1	3	3.94	92.2
2	3	0.26	6.1
3	5	0.07_5	1.7
1–3	11	4.27_5	100.1
Residue	69	0.00^5	0.0

Spin baths containing varying amounts of cyclohexylamine were analyzed. The composition of the bath was H_2SO_4 (122 g./l.), $ZnSO_4$ (79 g./l.), and Na_2SO_4 (305 g./l.).

Technical grade reagents, which are often contaminated by ammonium salts, were used. A blank must therefore be run. The following procedure is recommended.

Transfer 100 ml. of the spin bath containing cyclohexylamine to a 500-ml. flask fitted with a dropping funnel, a splash head, and a condenser set for downward distillation. Dilute with 100 ml. of water and add an excess of 10 *N* NaOH soln. (about 50 ml.) from the funnel. Heat to gentle boiling and collect 25 ml. distillate in a flask with an excess of 0.1 *N* HCl soln. The receiver adapter should end below the surface of the HCl soln. Back titrate with 0.1 *N* NaOH soln. Run a blank in the same way, using a spin bath with no cyclohexylamine added. Calculate the amount of amine from the difference between the blank and the sample.

The results from several runs are collected in Table II. The accuracy is evidently quite sufficient for practical purposes.

TABLE II. Determination of Cyclohexylamine (CHA) in 100-ml. Spin Bath

CHA added, g.	0.1000 *N* HCl soln.			CHA found, g.	Error	
	total ml.	blank ml.	corr. ml.		mg.	%
0.481	49.3	1.27	48.0	0.476	−5	−1
0.175	18.7	1.27	17.4	0.173	−2	−1
0.169	18.2	1.27	16.9	0.168	−1	−1
0.1390	15.10	1.27	13.83	0.1370	−2.0	−1
0.1006	11.22	1.27	9.95	0.0987	−1.9	−2
0.0453	5.72	1.27	4.45	0.0441	−1.2	−3
0.0430	5.54	1.27	4.27	0.0424	−0.6	−1
0.0243	3.65	1.27	2.38	0.0236	−0.7	−3

Literature Cited

1. Hiers, G. S. and Adams, R., *Ber. deut. chem. Ges.* **59**, 162 (1926).
2. U.S. Pat. 2,535,044; 2,535,045.

MAGNUS MATELL

Book Reviews

Polymer Solutions. H. Tompa. New York, Academic Press, and London, Butterworth Science Publications, 1956. 325 pages. Price $8.50.

Reviewed by H. Morawetz, Interscience Publishers, New York, New York

This monograph, written by one of the most thorough workers in the field, will be a welcome and most useful addition to the library of all those conducting research on polymer solutions. After some introductory material it contains chapters entitled "Theories of Polymer Solutions," "Vapor Pressures and Heats of Mixing," "Osmotic Pressure," "Phase Relationships," "Chain Configurations," and "Viscosity and Light Scattering." The author presents a mathematical treatment of his subjects in a detailed fashion distinguished by its clarity. There is, as is usual in such cases, a variation in emphasis, with the chapters on the theories of polymer solutions and on phase relationships obviously closest to the author's heart. This reviewer feels that Dr. Tompa's discussion of phase equilibria should be singled out for special praise.

The limitations in the scope of this book are clearly stated in the introduction. They are due to the author's expressed conviction that the interest of phenomena decreases in proportion as our understanding of them becomes less rigorous. This is a legitimate view, but surely not the only one that may be held on this matter. As a consequence, the author excludes from his volume not only all considerations of polyelectrolytes, but brushes off all effects due to polar group interactions, hydrogen bonding, etc. with the curt statement that "there is no reason to believe that these forces are different from those in nonpolymeric substance" (p. 3). The reader is thus not warned about the possibility of measuring different "aparrent molecular weights" in different media due to the persistence of molecular aggregation to extreme dilutions, or the profound effect on the properties of some polymer solutions due to very small concentrations of hydrogen bonding cosolvents.

In the discussion of ternary systems, two interesting cases have been omitted. The first consists of a polymer and two solvents which have a high affinity for each other so that a mixture of the solvents is a nonsolvent for the polymer (Gee, *Trans-Faraday Soc.*, **40**, 463). The other consists of a single solvent and two strongly interacting polymers, so that the polymers precipitate each other from solution. The impression is also conveyed (p. 197) that the solubility of polymers in mixtures of nonsolvents is always due to the averaging of their cohesive energy density. This takes no account of the failure of the cohesive energy density treatment for mixtures of polar solvents (Hildebrand and Scott) and the importance of specific group interactions in the solubilizing action of cosolvents.

The book contains very few errors. On page 62 the reference to Equation 3.2 should refer to 3.25. On page 246 "mean square end-to-end distance" should be substituted for "rms end-to-end distance," and Equation 8.11 on p. 239 should read "$s^2 = (1/r)\Sigma s_i^2$." On page 280 Alfrey et al. are misquoted, since their work dealt with various solvent-nonsolvent systems at a fixed temperature, as well as a single system over a temperature range. The physical interpretation of Raoult's law given on p. 58 is questionable, since in the limit of high dilution the number of solvent molecules in the surface layer will depend not only on the mole fraction but also the size of solute molecules.

In spite of the fact that some other recently published books deal with similar subject matter, there is no question in this reviewer's mind that the originality with which Dr. Tompa approaches some of the problems dealt with in his volume make it unique in many respects. It may be recommended wholeheartedly to all research workers in the field.

Wool Wax, Chemistry and Technology. E. V. Truter. Cleaver-Hume Press Ltd., London, Interscience Publishers, Inc., New York, 1956. Price $8.75.

Reviewed by Werner Von Bergen, Forstmann Woolen Co.

Dr. Truter's work is the first comprehensive critical review of wool wax and suint, byproducts of the wool fleece; occurrence, principles and methods of extraction, refinement and chemical processing, chemical constitution, extraction of biochemically important

components; physiological steroids and lanostane analogues; and principal uses.

At its outset, the author puts forth essential definitions on the natural byproducts of the fleece such as yolk, wool wax, suint, wool greese and lanolin. The first Chapter, The Fleece Contents, goes into detail in regard to the fleece contents, the relationship which exists between wax and suint content and wool qualities. The latest research on the function of wax and suints in the fleece is presented which shows that whereas wool wax does not seem to afford any protention against the influence of light, the protective action of suint in this regard has been established.

The Second Chapter, The Chemical Constitution of Wood Wax, is covered very thoroughly. Most valuable are the tables giving the melting points of the various wool wax acids present. Figures are also presented regarding the considerable variation which exists in the wool wax composition from different breeds of sheep.

Chapter 3, The Constitution and Uses of Suint, sheds new light on the yellowing effect suint may have on the wool and its possible physiological functions.

Chapters 4, 5, and 6 deal respectively with the important role of emulsions in industry; the recovery processes used today, including processes recently developed in Australia; and saponification of wool wax and separation of the major products of the reaction.

Chapter 7 deals with the Isolation and Determination of Cholesterol, which is by far the most valuable constituent. About half of the world's production of cholesterol is extracted from wool wax alcohols.

Chapter 8, Sorting Molecules by Size and Shape, moves into a technique which is still in its infancy, but enough is known already to indicate that it will eventually rank in importance with crystallization and distillation as a means of separating mixtures.

Chapter 9 deals with the Lonastane Derivatives compounds, which were only isolated within the past twenty years. The true importance of these groups of triterpenes has not yet been fully established but indications are that they may be of considerable biological importance.

The preparation of hormones from chlesterol and lanosterol, the Bradford recovery process and how the effluent from Bradford woolen mills is now made to pay the cost of the treatment; and the uses of wool wax in the various industries are discussed in the last three chapters in the book.

There are two appendices. Appendix I gives the location of single side chain methyl groups as they occur in wool wax. Appendix II describes the method of estimation of residual grease on the washed wools and wool tops, as has been recommended by the International Textile Organization.

The book is not only essential for all laboratories in the woolen and worsted industries and related fields, but in many industrial laboratories as well. In its excellent presentation of the complex chemistry of wool wax, it is of great interest to workers in such diverse fields as lipids, steroids and triterpenes, emulsions, and various aspects of pharmacy. It is a "must" for all chemical libraries, as well as for all allied government agencies.

Fibres, Plastics, and Rubbers: A Handbook of Common Polymers. W. J. Roff, New York, Academic Press, and London, Butterworth Scientific Publications, 1956. xvi + 400 pages. Price $10.00.

Reviewed by W. James Lyons, Textile Research Institute, Princeton, New Jersey

Intended as a directly practical work of reference, this book has achieved well the author's objective. The volume is divided into two parts, the first of which consists of 38 concise chapters (called "tables," though they have the ordinary textual format), each devoted to an individual commercial polymer. For chapter headings common generic names (silk and wool, rubber), or when these do not exist, applicable chemical terms (polyamides, polytetrafluoroethylene) are used. Uniformly, in each chapter are given synonyms and trade names, available information on structure, molecular weight, and x-ray pattern. There follow sections outlining the basic chemistry of the commercial product, chemical properties, methods of identification, physical properties (generally with tables), serviceability and utilization, and a thumbnail history. Most chapters have sections of additional notes and references.

In the second part of the book are 34 chapters (also called "tables"), each devoted to a specific property or group of related properties, or to information of a general nature, such as the preparation of polymers and their identification. In this part are numerous tables giving the ranges of values of properties for the various polymers, as well as for materials such as metals and alloys, which are not treated in the first part of the book. Thus is the volume so planned that the user may consult it to

find some item of information concerning a particular fiber or polymer, or to find materials which satisfy particular requirements with respect to one or more properties, for instance, a range of values. The subject of the identification of polymers, which appears in both parts of the book, is treated very thoroughly.

Unfortunately, so rapid has been the progress of polymer science, though the book was published January 24, 1957, it contains nothing on the new isotactic polymers or the synthetic all-*cis* polyisoprene ("Artificial synthesis of rubber has not been achieved"). Similarly lacking is information on the new vinylidene dinitrile/vinyl acetate (Darlan) and nitrile "alloy" (Zefran) fibers. Strict adherence to the author's plan of devoting no more than one chapter to each macromolecule has resulted in the somewhat artificial lumping together of cotton, bast fibers, rayons, and cellophane.

While the Textile Institute of Great Britain has acted as an intermediary in the publication of *Fibres, Plastics and Rubbers,* the book should be found to be as useful to scientists and technologists in the plastics and rubber industries as to those in the textile field.

Organic Synthesis. Vartkes Migrdichian. New York, Reinhold Publishing Corp., 1957. Two volumes, 1822 pages. Price $35.00.

Reviewed by Richard K. Hill, Department of Chemistry, Princeton University, Princeton, New Jersey

In these two volumes Dr. Migrdichian has undertaken a complete survey of organic synthetic methods. The result is a remarkably thorough book, containing a wealth of information.

In scope, it falls between the one-volume summary of Wagner and Zook and the comprehensive treatment of Houben and Weyl. It is organized like a textbook, discussing general methods in great detail and listing many specific examples of important reactions. An idea of the detail may be gained by noting the 80 pages on the Grignard reaction, 100 pages on organometallic compounds, 53 on the diene synthesis, 50 on carbohydrates, and 57 on diazonium compounds. Such newer fields as azulenes and steroid synthesis receive excellent coverage. Heterocyclic compounds are left to a third volume, and no attempt is made to treat theoretical aspects of reaction mechanism and stereochemistry.

Several drawbacks detract from the book's usefulness. It contains a great many errors that careful proofreading should have caught. It repeats inaccuracies from the older literature: the cyclic azide structure, the 9,10-bonded formula for anthracene, a terpene structure which violates Bredt's rule. More important, it fails to list many of the newer methods which one might expect in a 1957 publication; the Wittig olefin synthesis, polyphosphoric acid, and dehydrations with dicyclohexylcarbodiimide are not mentioned. Neither are the Prevost reagent, Cope's excellent method for cyanocetic ester condensations, nor three of the good methods for preparation of keto-acids (Fieser's oxidation of cyclic tertiary alcohols, ring opening of furan alcohols, and alkyl nitrite cleavage of alkyl cyclic ketones). Finally, one wonders at the organization which capriciously divided both aldehyde synthesis and carbonyl reduction between two separate chapters.

Nevertheless, this is a valuable reference work. While few organic chemists can afford to buy it, all of them will enjoy and profit by its use.

THE INDEX

TO THIS VOLUME HAS BEEN REMOVED FROM THIS POSITION AND PLACED AT THE BEGINNING OF THE FILM FOR THE CONVENIENCE OF READERS.

find some item of information concerning a particular fiber or polymer, or to find materials which satisfy particular requirements with respect to one or more properties, for instance, a range of values. The subject of the identification of polymers, which appears in both parts of the book, is treated very thoroughly.

Unfortunately, so rapid has been the progress of polymer science, though the book was published January 24, 1957, it contains nothing on the new isotactic polymers or the synthetic all-*cis* polyisoprene ("Artificial synthesis of rubber has not been achieved"). Similarly lacking is information on the new vinylidene dinitrile/vinyl acetate (Darlan) and nitrile "alloy" (Zefran) fibers. Strict adherence to the author's plan of devoting no more than one chapter to each macromolecule has resulted in the somewhat artificial lumping together of cotton, bast fibers, rayons, and cellophane.

While the Textile Institute of Great Britain has acted as an intermediary in the publication of *Fibres, Plastics and Rubbers,* the book should be found to be as useful to scientists and technologists in the plastics and rubber industries as to those in the textile field.

Organic Synthesis. Vartkes Migrdichian. New York, Reinhold Publishing Corp., 1957. Two volumes, 1822 pages. Price $35.00.

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